

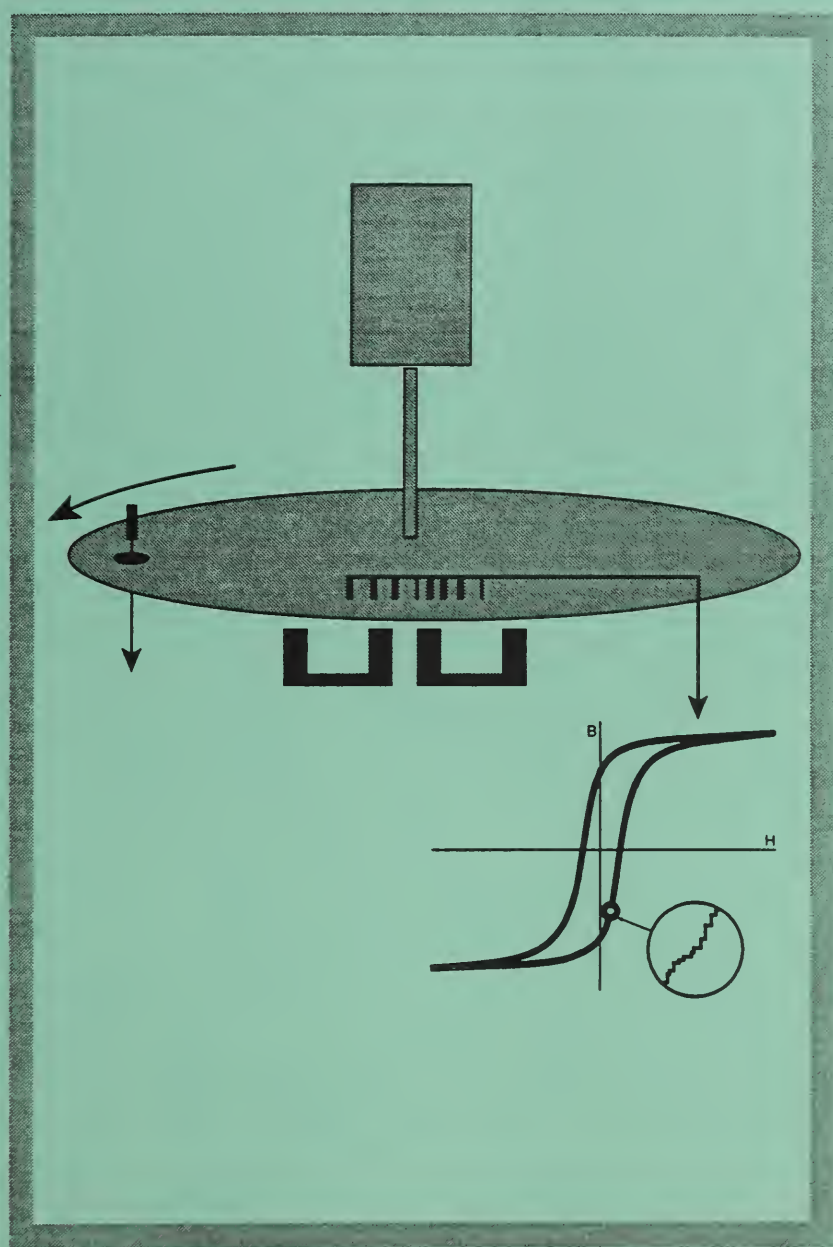


Materials Science and Engineering Laboratory

INTELLIGENT PROCESSING OF MATERIALS

NAS-NRC
Assessment Panel
April 6-7, 1995

NISTIR 5578
U.S. Department of Commerce
Technology Administration
National Institute of Standards
and Technology



Technical Activities 1994

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Cover:

Magnetic Barkhausen testing of the properties of moving sheet steel.

Materials Science and Engineering Laboratory

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D.E. Hall, Chief
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Certain companies and commercial products are mentioned in this report. They are used to either completely specify a procedure or describe an interaction with NIST. Such a mention is not meant as an endorsement by NIST or represent the best choice for that purpose.

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INTRODUCTION

Intelligent processing of materials (IPM) includes the application of sensors, process models, data/knowledge bases, and on-line controllers to adjust process conditions in real time to achieve a desired result, which is usually a defined set of materials characteristics and properties. IPM is a technical area of opportunity with great leverage and is a key to the cost-effective manufacture of high-quality materials.

The Office of Intelligent Processing of Materials (OIPM) is concerned with all aspects of intelligent processing. Our primary focus is on process sensors, which our industrial collaborators repeatedly identify as a crucial need. Our sensor research and development is aligned with NIST's role in measurement technology and is a natural outgrowth of OIPM's work in nondestructive evaluation of materials. In recent years, the office has sponsored more process modeling research, and, when necessary, development of integrated IPM systems.

Our programs fall into two categories. We form and join consortia and other large programs to accelerate research progress and transfer technology to our industrial partners. These large programs often involve NIST, industrial, university, and other government researchers in multi-disciplinary research teams. In addition, we sponsor several smaller sensor research projects to investigate the feasibility of advanced sensor techniques in specific applications.

This year, two major OIPM programs completed research work and moved into plant demonstration or implementation phases. The consortium on intelligent processing of rapidly solidified metal powders met its technical targets, successfully demonstrating pilot plant production of metal powder in a fully instrumented system under intelligent control. Work will continue in 1995 to transfer the technology to consortium members. We also reached agreement with the Aluminum Association and member companies to conduct a definitive plant trial of an eddy current sensor system for accurate measurement of aluminum temperature during hot rolling. The plant trial of the NIST sensor is scheduled for June 1995.

NIST researchers also made a number of significant scientific and technical advances in other IPM programs this year. These technical advances include the following:

- The electrical resistivities of a superalloy and a titanium alloy, used for casting jet engine components, were measured at temperatures ranging up to several hundred degrees above their liquidus temperatures. These measurements provide resistivity values 2-3 times more accurate than those previously available.
- A heat transfer model of the shielded metal arc welding process was developed that predicts the consumed length of the electrode. This model can be used for weld schedule design.

- An optical sensor was designed and used to obtain real-time measurements of fluorescence anisotropy during extrusion of polycarbonate doped with perylene. This result is an important step toward real-time determination of stress during processing.
- A new instrument was constructed that records both the light scattering images of polymers under shear and the microscopic images of polymers under flow in real space. The instrument is a significant advance for studying polymer behavior under shear.
- Studies of the surface chemistry and interactions in the sintered, reaction-bonded silicon nitride system demonstrated and characterized the unstable nature of silicon powders in suspension. This work clarified important aspects of the aging process and showed the need to control aging effects during processing.

The Office of Intelligent Processing of Materials also launched a new NIST distributed Center for Theoretical and Computational Materials Science in 1994. The purpose of the center, which includes researchers at NIST and other institutions nationwide, is to stimulate the development of theory and modeling in materials research and their application to industrial materials problems. The center has developed an active research agenda and has promoted the formation of research teams in several materials areas. In addition, the center operates a materials theory information server on the World Wide Web to promote electronic information exchange and research collaboration. More information about the materials theory center is available from this office or on the server at <http://www.ctcms.nist.gov>.

The technical programs of the Office of Intelligent Processing of Materials are focused on the materials processing needs of American industry. Our programs are developed with extensive industry consultation, and the technical agenda and goals are discussed on a continuing basis with our industrial collaborators. The office welcomes ideas for new IPM programs with the potential for substantial industrial impact in the areas of metals, ceramics, polymers, composites, and advanced materials. For more information on the projects in this report, contact the individual investigators or the Office of Intelligent Processing of Materials, Materials Building, Room B344, National Institute of Standards and Technology, Gaithersburg, Maryland 20899 (301-975-5727).

Dale Hall, Chief
Office of Intelligent Processing of Materials

Intelligent Processing of Rapidly Solidified Metal Powders by Inert Gas Atomization

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This report is a summary of fiscal year 1994 activities of research on metal atomization which began more than nine years ago when metal powder was first produced in the Metallurgy Division's SiGMA (Supersonic inert Gas Metal Atomizer) system. During this time period several atomization studies involving sensors, diagnostics, and control were initiated. Two consecutive, three-year research programs were most recently completed. The first, or Phase I, NIST/US industry consortium directed activity, ending in July 1990, resulted in the necessary modeling, sensor, control equipment, personnel, and resolve to pursue the more ambitious Phase II activity. The Phase II consortium (outlined in the 1991 IPM annual report) was focused on real-time particle size sensing and control. This consortium was initiated using cooperative research and development agreements, direct contracts, and/or work requests with Ampal/Metallurg, Crucible Materials Corporation, DOE - Office of Industrial Processes, General Electric Aircraft Engines, Martin Marietta Energy Systems, Inc., and United Technologies - Pratt & Whitney. The overall research goal was to atomize Inconel alloy 625 with expert system control incorporating a feed-back loop. As a consequence of the accomplishment of this goal (in March of 1994), several subsystems and methodologies were made available to the consortium members. These technologies include the Expert Control System Shell (ECSS) code that runs on Macintosh computers, the particle sizing code written in C language and the Computational Fluid Dynamics (CFD) code written in Fortran for compatibility with most computer systems. These and other technologies have evolved as needed to meet project objectives (updates are continuously available). Workshops were used to transfer these technologies to the consortium members. The first of these single-purpose tutorials (on particle sizing) was held during fiscal year 1992 at NIST. The second workshop covering the use of the NIST CFD model for solving supersonic gas flows was held June 8-9, 1993.

In this reporting period, work on the Fraunhofer diffraction instrument (used as the in-situ, real-time powder sizing sensor for SiGMA) focused on the inversion of diffraction data to obtain a Particle Size Distribution (PSD). The details of this measurement technique, including the mathematical theory and optical geometry, are available in previously published

papers. [1,2] In summary, this instrument produces a collimated HeNe laser beam that passes through a set of view-ports located upstream of the cyclone separators used to remove the metal powder from the process gas. Powder particles passing through the illuminated volume between the view-ports scatter the laser beam at characteristic angles and intensities relative to their diameters. The scattering data are in the form of 32 light intensity values; one measuring undiffracted light that is focused through a hole in the detector array panel and onto a centrally located photo diode, and the rest measuring light diffracted to individual semi-circular photo diodes arranged in a "rainbow" pattern across the diffraction plane. The data are acquired at a 2 Hz sampling rate concurrent with several analog and digital signals from transducers and actuators measuring pressures, temperatures, incandescence of molten metal spray, valve positions, etc. located throughout the process plumbing. The result is a time signature (in the form of diffraction intensities) of the dynamic response of the SiGMA system. Control strategies can be devised directly from this diffraction data once sufficient knowledge of the relationship between diffraction and PSD is obtained. This knowledge has been acquired by developing and using various inversion algorithms derived from diffraction theory. Recent studies were aimed at comparing PSD's obtained from diffraction data to those obtained from sieve data using data generated from well-characterized and controlled (in terms of the currently available process sensors and actuators) atomization runs.

Various process conditions were selected to provide powder product that represented the extent of the SiGMA processing envelope. The process flow from the SiGMA system passes through cyclone separators (immediately downstream from the particle sizing view-ports). The powder falls into cans at the bottom of the separators while the processing gas flows downstream to be exhausted through industrial vacuum cleaners equipped with HEPA filters. During each selected atomization run the processing conditions were monitored and allowed to stabilize. When the desired processing conditions were achieved, the powder product was diverted to a sampling container to isolate it from the rest of the powder product. The "sample" powder was analyzed by an industry-standard, acoustic air column sieving apparatus. The resulting sieve data (mass percent of total "sample" powder in 18 different particle diameters from 5 to 250 μm) was compared to PSD's generated by inversion of the diffraction data corresponding to the same time period during which the powder was collected.

The results of this study indicate that PSDs of atomized metal powder can be generated in-situ from scattered light data. The reliability and accuracy of this sizing technique depend on special process flow conditioning devices developed by the NIST participants during this consortium research project. These devices improve the homogeneity of the powder/gas mixture and reduce refraction of laser light caused by temperature gradients. Special inversion techniques, also developed by NIST, are required to convert the diffraction data into PSDs. A discrepancy is still seen between sieve-generated PSDs and those from diffraction (sieve data on SiGMA produced alloy 625 powder show multimodal peaks whereas diffraction data usually indicate a single maximum in the PSD); however, correlation of average particle diameter statistics is consistent and predictable.

Another sensor development activity focused on the determination of the liquid metal flow rate. Techniques investigated included 1. strain sensors to measure mass change of crucible; 2. inductive core loss; 3. continuous mass sensing with γ or x-rays; 4. eddy current sensing of metal flow through the metal delivery tube; 5. use of an argon bubbler tube to measure metallostatic head in the crucible; and 6. deductive calculation from other sensor data. Techniques 1. through 3. were discussed in the 1993 report. These were either ineffective or not tested (purchase price was prohibitive). Techniques 4. through 6. have received considerable attention. The details regarding eddy current sensing were discussed in last year's report and several publications [3-5]. Results to date have been limited to "bench-top" tests using a closed mercury flow system. Current sensor size precludes trial in the SiGMA system, and further work is required to test performance in the presence of magnetic fields such as those generated by induction melting equipment.

The essential design components of the argon bubbler tube to measure metallostatic head in the crucible are shown schematically in Figure 1. The principle of operation is a simple and commonly used technique employing a "bubbler tube" to measure the total static head pressure within the alloy crucible [6]. As currently configured, the ceramic bubbler tube connects to a gas supply regulated to a pressure just above that required to produce bubbles in a full crucible with maximum chamber over-pressure. In SiGMA the maximum over pressure is ≈ 124 kPa (18 PSIA) and the static pressure of 240 mm (9.5") of alloy 625 is ≈ 19 kPa (2.8 PSIA). Therefore, the bubbler gas supply requires ≈ 143 kPa (21 PSIA). A differential pressure transducer between the melt chamber and the bubbler supply is used to measure the melt static pressure. Figure 2 shows data from one of the recent atomization runs where a bubbler tube was used. The high frequency "noise" in this curve results from the formation of individual bubbles at the bottom of the ceramic tube. The lower frequency "dips" appear to be associated with periodic pressure changes occurring within the melt chamber as the melt chamber pressure control valves are opened and closed. These melt chamber pressure fluctuations are not as severe as indicated in these data but most likely result from a combination of the high sensitivity of the differential pressure transducer (100 inches of H_2O or ≈ 25 kPa full scale) and the higher damping factor in the measurement plumbing leading from the bubbler to the "high" pressure port compared to the plumbing running from the melt chamber to the "low" pressure port of the transducer.

Advantages of this technique include the simplicity of components and the relative ease of installation. Drawbacks that are known include its limitation to bottom-pour installations, complexities involved with the tube that must withstand exposure to the molten 625 alloy, the data "noise" resulting from the relatively high sensitivity of the pressure transducer, and dependence on well-defined crucible profiles (leaks and shape changes in the crucible degrade resolution). The requirement for bottom pouring can be relaxed to accommodate systems that tilt-pour into a bottom pour tundish if an intermittent pour procedure is used. (Flow measurements would be interrupted when filling and commence after each crucible refilling cycle.)

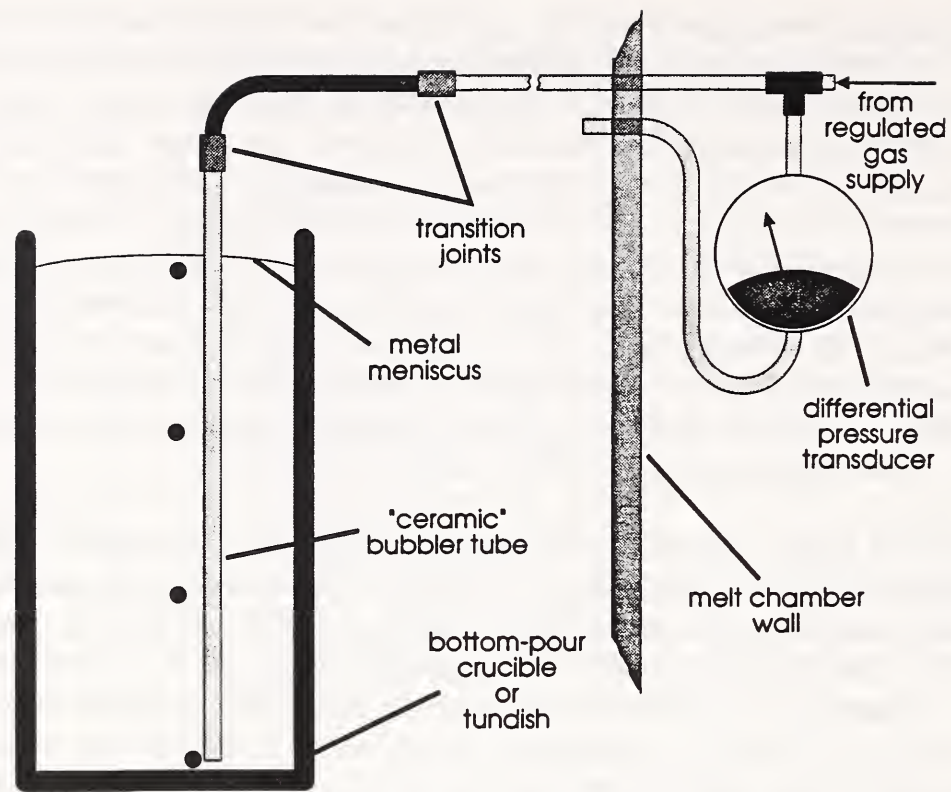


Fig. 1. Schematic drawing of "bubbler tube" metallostatic head sensor.

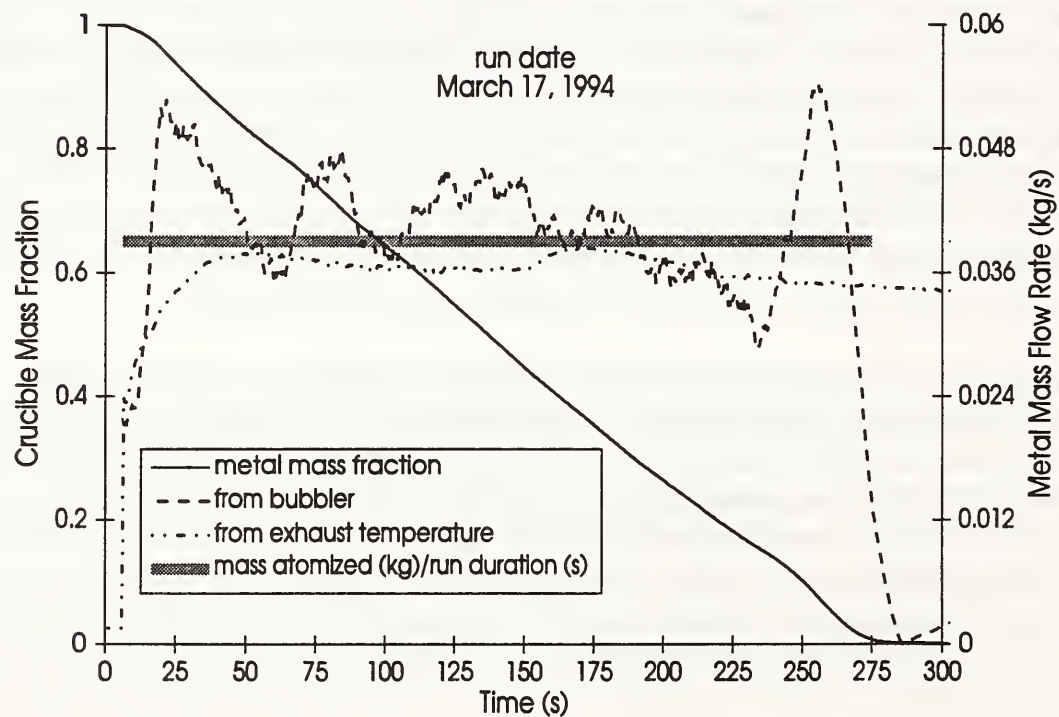


Fig. 2. Metal mass-flow rate calculated from the bubbler tube and the exhaust gas temperature.

Metal flow rate by deductive calculation from other sensors uses either the exhaust gas temperature and/or the particle sizing laser obscuration and mathematical correlations to compute the desired quantities. The available obscuration data from the particle sizing sensor measures the total quantity of scattered light and varies as a function of total projected surface area of powder within the illuminated column. A potential problem that renders this technique unattractive is the required correction needed to account for effects of particle size distribution (a quantity of "small" powder would scatter more light than an equal mass of "large" powder). Also, the laser obscuration signal normally seen during the atomization runs was judged to display more apparent noise than the exhaust gas temperature and, therefore, this sensor signal was not analyzed further.

The exhaust gas temperature strongly depends on both atomizing gas and liquid metal flow rates. The effects of heat loss to the chamber walls and changes in metal superheat are the only known major sources of error. Transient response is tied to the flight time from the metal delivery tube to the bottom of the atomizing chamber (where gas temperature is measured) and to the response time of the thermocouple. These times combined are less than 0.25 s and should not cause a problem. Since the gas mass-flow rate is currently measured, metal flow rate can be calculated from heat capacity and heat of fusion data using an energy balance. This results in the following equation

$$\dot{m}_m = \dot{m}_g (C_{pg}(T_{exh} - T_e + (v_{exh}^2 - v_e^2)/2) / (H_{fm} + C_{pm}(T_1 - T_{exh}) + (v_1^2 - v_{exh}^2)/2) \quad (1)$$

Where \dot{m}_m is the metal mass-flow rate (MMFR), \dot{m}_g is the gas mass-flow rate (GMFR), C_{pg} is the constant pressure heat capacity of the gas (assumed constant with temperature), T_{exh} is the exhaust gas temperature, T_e is the temperature of the gas jets as they exit the die, v_{exh} is the velocity of the exhaust gas, v_e is the velocity of the gas jets as they exit the die, v_1 is the velocity of the metal as it leaves the delivery tube, H_{fm} is the heat of fusion for the metal alloy, C_{pm} is the constant pressure heat capacity of the metal (assumed constant with temperature and phase change), and T_1 is the temperature of the metal when it leaves the metal delivery tube.

This energy balance assumes that there is no net accumulation of gas or metal in the atomizing chamber ($\dot{m}_g|_{in} = \dot{m}_g|_{out}$ and $\dot{m}_m|_{in} = \dot{m}_m|_{out}$); that negligible heat is transferred to the chamber walls, etc.; that the powder and gas are the same temperature as they exit the atomizing chamber; and that C_p is not a function of temperature or phase change. The assumptions of constant C_p for the gas and the metal, although incorrect, are sufficiently accurate concerning the accuracy of the C_{pm} data and the nature of the raw data itself. The value of C_{pg} is fairly well known (for Ar a value of 520.84 J/(kg K) was used) while H_{fm} and C_{pm} are still in question. The average metal mass-flow rate (total metal mass poured divided by the total pour time) was used to adjust these values until reasonable agreement was reached. The value for H_{fm} was found to be 170 J/kg and the value for C_{pm} was found to be 590 J/(kg K).

Figure 2 shows the results of calculations made on post run data from one of the atomization runs. In this figure the solid curve shows the decreasing metal mass fraction held in the crucible based on a static pressure measurement using a bubbler tube, the dashed curve shows the MMFR from this same sensor, the dot-dashed curve is the MMFR calculated from the exhaust temperature using equation 1 and the thermal data discussed previously, and the wide "gray" line is the MMFR calculated from the mass of metal atomized divided by the run duration. As can be seen from this figure the MMFR calculated from the exhaust temperature is significantly less noisy than the bubbler tube-derived MMFR, and experience has shown very high reliability in the exhaust gas thermocouple temperature sensor.

A parameter often used to describe the operation of gas atomizers is the gas mass-flow to metal mass-flow ratio (usually referred to as Gas to Metal Ratio or GMR). From equation 1 it can be shown that

$$\begin{aligned} \text{GMR} &= (H_{\text{fm}} + C_{\text{pm}}T_1 + (v_1^2 - v_{\text{exh}}^2)/2 - C_{\text{pm}}T_{\text{exh}})/(C_{\text{pg}}T_{\text{exh}} - (C_{\text{pg}}T_c + (v_c^2 - v_{\text{exh}}^2))) \\ &= (K_{\text{tp1}} - K_{\text{tp2}}T_{\text{exh}})/(K_{\text{tp3}}T_{\text{exh}} - K_{\text{tp4}}) \end{aligned} \quad (2)$$

where K_{tp1} , K_{tp2} , K_{tp3} , and K_{tp4} are constants calculated from the thermal properties of the atomizing gas and alloy being atomized. ($K_{\text{tp1}} = H_{\text{fm}} + (C_{\text{pm}}T_1) + (v_1^2 - v_{\text{exh}}^2)/2 \approx 916.6$ (kJ/kg), $K_{\text{tp2}} = C_{\text{pm}} \approx 0.44$ (kJ/kg K), $K_{\text{tp3}} = C_{\text{pg}} \approx 0.52$ (kJ/kg K), and $K_{\text{tp4}} = C_{\text{pg}}T_c + (v_c^2 - v_{\text{exh}}^2) \approx 56.56$ (kJ/kg) for Ar gas and alloy 625 metal.) In other words, maintaining a constant exhaust temperature while atomizing an alloy poured at constant temperature insures a constant GMR. The control strategies that could achieve this exhaust temperature control will depend on a particular atomizer's design.

Process modeling during this fiscal year focused on CFD analysis of gas-only supersonic flow in the atomizing jets and the energy balance work associated with the metal flow rate sensor. Results of these studies include the gas-only CFD code (mentioned previously regarding focused subject workshops) and the calculation of metal flow rate discussed in the preceding section. This has lead to incorporation of the GMR into the list of real-time acquired parameters. The CFD code was used by one consortium member to help redesign their commercial metal atomizer resulting in dramatic cost savings from reduced argon gas consumption.

The current CFD studies are focused in four major areas: adaptive grid technology; viscous stress modeling; effects of liquid delivery tube extension; and turbulence stress modeling. All of these areas are associated with improving the predictive capabilities of the CFD code. Work is continuing in each of these areas with particular emphasis on the turbulence stress modeling. Difficulties were found that are associated with the current "state of the art" in turbulence models and the boundary conditions used in the coupling of flow between the supersonic jet flow with the subsonic "aspiration" region where the metal first interacts with the gas. As these problems are solved, it is hoped that predictive

calculations of metal aspiration (the "base" flow average pressure that strongly influences the metal flow rate) will be possible.

The SiGMA ECSS control system was used extensively in the last two years to precisely control the operation of the atomizer as required in the particle sizing and metal flow rate sensor work, reported previously, as well as for the "Experimental Run Matrix", reported in last year's report. In addition, an operating manual for the ECSS was written that describes in detail the installation and operation of this software on a Macintosh computer. This manual is available to consortium participants as a chapter in the final report of the NIST/US industry consortium research program on gas atomization and as a document that will be published separately for the public after it passes the review process.

The ECSS controlled experiments were also used to establish a relationship between the **GMR** and the particle size produced by SiGMA as an extension of the "Experimental Run Matrix" work. The variables chosen for the matrix experiments were derived from a dimensional analysis of gas atomization. Two reasons can be cited for not choosing **GMR** as a factor in this matrix: a **GMR** sensor was not available when the experiments were conducted (the relationship between the exhaust gas temperature and **GMR** had not yet been determined); and it was assumed (or more accurately, hoped) that the **GMR** would be determined by fixing the other factors. This later "reason" depended on the precise reproducibility of several "fixed" quantities and factors that influence the metal or gas flow rates. These included (but were not limited to) the geometric alignment of the gas jets and the metal delivery tube, the bore diameter and finish of the metal delivery tube, and the leak rate between the melt chamber and the atomizing chamber.

The exhaust gas **GMR** sensor discussed previously provided a means to employ **GMR** as an alternative to the other factors used in the matrix runs and thus determine a more predictable processing response function for the SiGMA system. Exhaust gas temperature data were used with equation 2 to calculate the **GMR** (as a function of time) for the atomization runs employed in the matrix. These time-dependent **GMR** values were used to calculate the average **GMR** during the time interval when powder was being sampled. The particle size data from the sampled powder is plotted against these average **GMR** values in Figure 3.

The data shown in Figure 3 clearly indicate a correlation between **GMR** and particle size. In this figure D50 refers to the volume or mass median diameter (50 percent of the powder by weight is of a diameter less than the D50 value). $D(3,2)$ refers to the Sauter Mean diameter (the diameter of a sphere with the same ratio of surface to volume as that measured from the entire distribution). PR refers to the dimensionless pressure ratio of the gas jets where $PR = P_0/(\gamma P_r)$, P_0 is the stagnation pressure measured in the gas jet supply upstream relative to the jet exit, and P_r is the reservoir or atomizing chamber pressure. The D50 value is particularly sensitive to **GMR** between the values of 3.0 and 5.0 with a hint of leveling off at **GMR** values above 5.0. The $D(3,2)$ value, although less strongly affected by **GMR**, shows significantly less scatter than the D50 value.

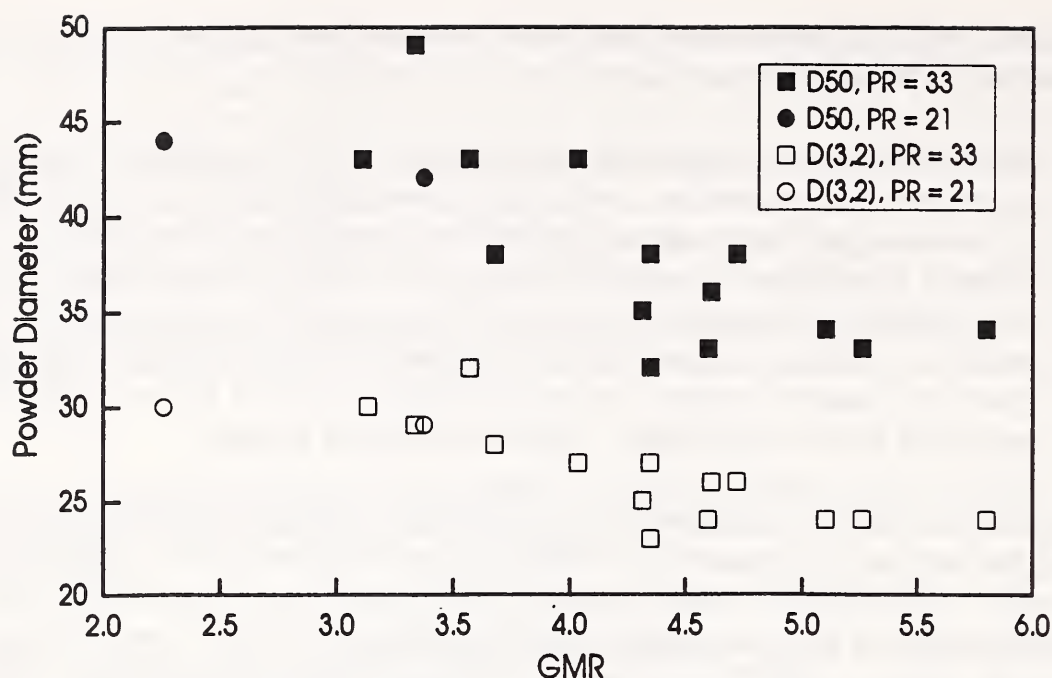


Fig. 3. Scatter diagram of the D50 and D[3,2] particle size values from sieve data plotted against the corresponding GMR value.

The successful completion of this project, as demonstrated by the atomization of 28 kg of alloy 625 using the automatic control system, resulted in an extension of this project to transfer this technology to a factory production facility. Recent advances in personal computer hardware and software will facilitate this task and should result in a simple, robust, and inexpensive process controller capable of performance levels equal to or better than the system used on SiGMA.

Modeling of fluid flow (both liquid and gas) with the CFD code generated during this project should be pursued with an emphasis on the modification of the atomization geometry to improve the size distribution (narrow size spread and/or reduced median size). Efforts in this area could be directed toward improved efficiency (lower GMR) by enhancing the sheet formation in the liquid flow prior to gas impingement. Another area that should be studied is the use of gas mixtures (Ar + N₂). Reactive gases like N₂ if trapped in the droplets during atomization will be absorbed into the metal matrix rather than forming bubbles as often seen in Ar-atomized droplets greater than 60 μ m.

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Casting of Aerospace Alloys

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Metal castings for use in aerospace applications must meet stringent quality requirements and at the same time must be produced on schedule and at competitive costs. Traditional methods of designing a casting process, which may involve processing several test castings and evaluating their microstructure, can take many months and involve high costs. Defects, which lead to rejection of the parts, can be present in a large fraction of the samples. The Consortium on Casting of Aerospace Alloys links NIST to companies in the aerospace industry and to universities and government agencies in a program to alleviate these problems by instilling more advanced materials science into the metal casting process.

The Consortium's research effort is distributed among its members, thus making it possible for each to take best advantage of its equipment, capabilities, and resources. In the last year, contributions by industrial members (Howmet Corp., PCC Airfoils, GE Aircraft Engines, United Technologies - Pratt & Whitney, Allison Engine, Allied Signal, and UES, Inc.) have included pouring and analyzing instrumented test castings, producing special samples for thermophysical property measurements, releasing their own data on thermophysical properties, and providing and using computer modeling software. Government agencies and non-profits (NASA, Bureau of Mines, Idaho National Engineering Labs, and American Foundrymen's Society) have provided financial support for research or carried out their own research projects, and have provided linkages to other casting research activities. University members of the consortium (Auburn University, Case Western Reserve University, CINDAS/ Purdue University, Massachusetts Institute of Technology, Pennsylvania State University, University of Alabama, University of Arizona, University of Illinois, and Worcester Polytechnic Institute) carried out both theoretical analyses of metal casting and experimental measurements, although not all have found financial support. This report emphasizes the NIST activities, all of them coordinated with other Consortium members, but there are several additional projects being carried out at other member institutions.

The industrial members of this consortium are primarily concerned with the production of aircraft engines and their components. The alloys of interest are therefore mostly nickel-based superalloys and titanium alloys, and the consortium's work addresses some of the

special problems that arise when working with these alloys. For example, superalloys of many different compositions have been developed, each of which normally contains a large number of constituent elements. The solidification behavior of most of these alloys is therefore only very poorly known. Moreover, unlike other alloy groups, superalloy castings often are produced in the form of single crystals, so they have especially stringent quality requirements. In the case of titanium castings, the reaction between the highly reactive metal and the mold causes difficulty in dimensional control.

A central part of this program's approach is modeling of the casting process, which allows one to make test castings on the computer and evaluate the results of the predictive models for microstructure and defect formation. Within the consortium, this modeling is carried out by the ProCASTTM commercial software package, which is a product of UES, Inc., one of the consortium's six industrial members. Much of the consortium's work is aimed at improving the scope of this software by enabling it to predict more details of microstructure and defect formation. This work includes components that are common to many intelligent processes for materials manufacture: refinement of models to describe microstructure development, measurement of thermophysical properties needed to evaluate the models, development of in-situ sensors to monitor the casting process in real time, and validation of the models, in this case by pouring of instrumented test castings. NIST workers collaborate with the consortium's industrial and university members in all of these areas, so that the industrial facilities for making castings are combined with the capabilities for sample analysis and model development at government laboratories and universities.

A basic requirement for heat flow modeling of castings is a knowledge of the fraction solid versus temperature relationship in the dendritic "mushy zone" between the liquid and the totally solidified metal. This relationship describes how the latent heat is evolved over the freezing range of the alloy. A general approach to this knowledge can be developed by combining multi-component phase-equilibrium diagrams with diffusional models for dendritic solidification. Results were obtained for a widely-used, eight-component alloy (IN718) by use of a Scheil analysis, which assumes that the liquid composition is uniform at each temperature and that diffusion is absent in the solid. The analysis used a preliminary thermodynamic model for the liquid-solid equilibrium concentrations at each temperature in the freezing range. With this model, the solidification of the face centered cubic (fcc) Ni solid solution is predicted to begin at 1334 °C, in close agreement with differential thermal analysis (DTA) measurements and metallographic examination. The model also predicts how the concentrations of individual elements change in the liquid phase of the mushy zone, as shown in Figure 1. This type of information enables the modeler to understand solute segregation patterns within the casting.

The thermodynamic model also can be used for other superalloy compositions for which there is an adequate database. Therefore, the database is being refined through an in-depth examination of the Ni-Cr-Fe-Nb quaternary system. The thermodynamic model was incorporated into a subroutine of computer code that is available for a variety of models more complex than the Scheil analysis of the solidification path.

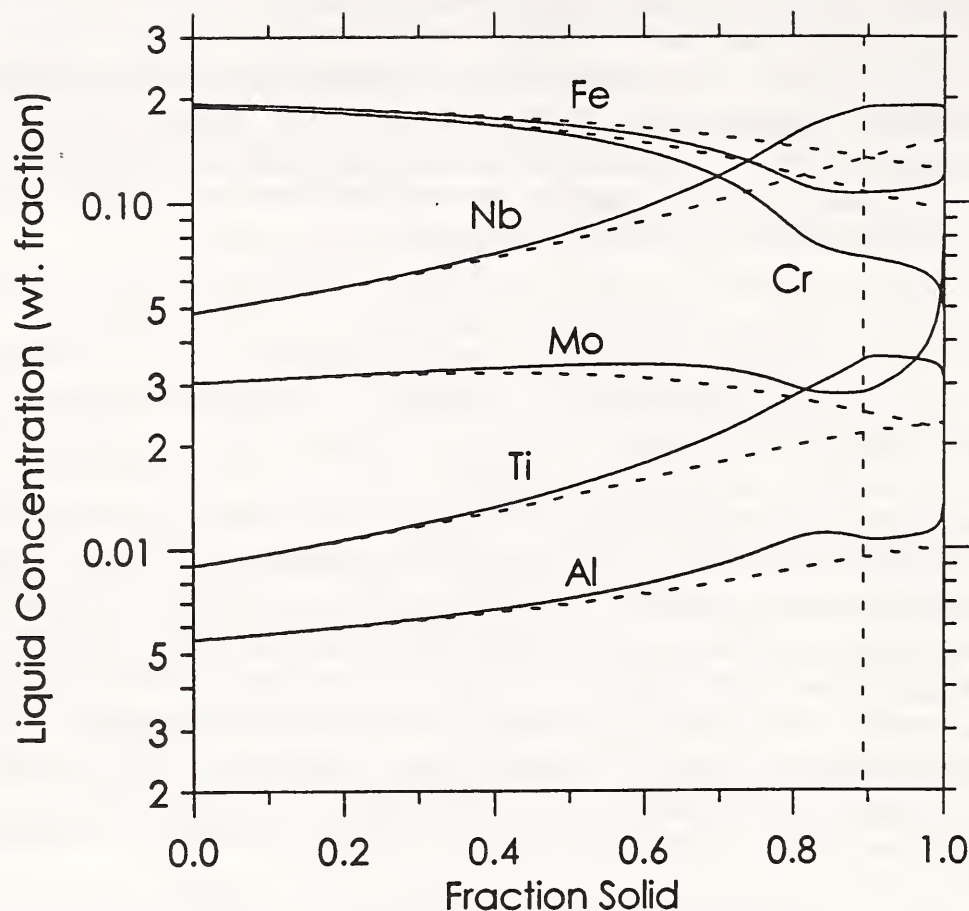


Fig. 1. Liquid concentrations of various elements as a function of fraction solid in the mushy zone for commercial alloy IN718. Co and Ta results are omitted for clarity. Predictions are made using a thermodynamic phase diagram mode coupled to a Scheil model of microsegregation. Other results, shown dashed, come from the lever rule which does not properly treat solidification. The vertical line is where the eutectic starts for the Scheil results.

Single crystal superalloy turbine blades must be rejected if they contain even minute regions of misorientation, significantly increasing the cost to the manufacturer. To understand the origin of such defects, we are examining their crystallography using samples provided by the Consortium's industrial members. In addition, we are modeling the thermal and crystallographic aspects of dendrites growing in molds of complex shape. Figure 2 shows an example of the predicted shape of a dendrite front emerging from a small opening into a wider part of a casting. This model can be used to predict the regions in which the growth rate is much higher than normal, leading to increased probability of defect formation.

The analysis has already identified the mechanism and approximate conditions of formation of one type of defect, known as a "zebra" grain. This identification provides a rational basis for steps that are known to be effective at reducing the incidence of such defects. Work is now directed toward a more quantitative identification of the conditions leading to formation of this type of defect, and study of additional defect types has been started.

A sensor that could monitor the position of the solidification front in single-crystal castings would have great value in validating models of the solidification process. Such a sensor, using x-rays to penetrate the mold wall and image the growing crystal, is under development and has shown considerable promise. Its operation was demonstrated in the laboratory on several metals, and plans are now in progress to test it on an actual superalloy. A patent application is currently being prepared, and more details of the sensor's operation will be given in next year's report.

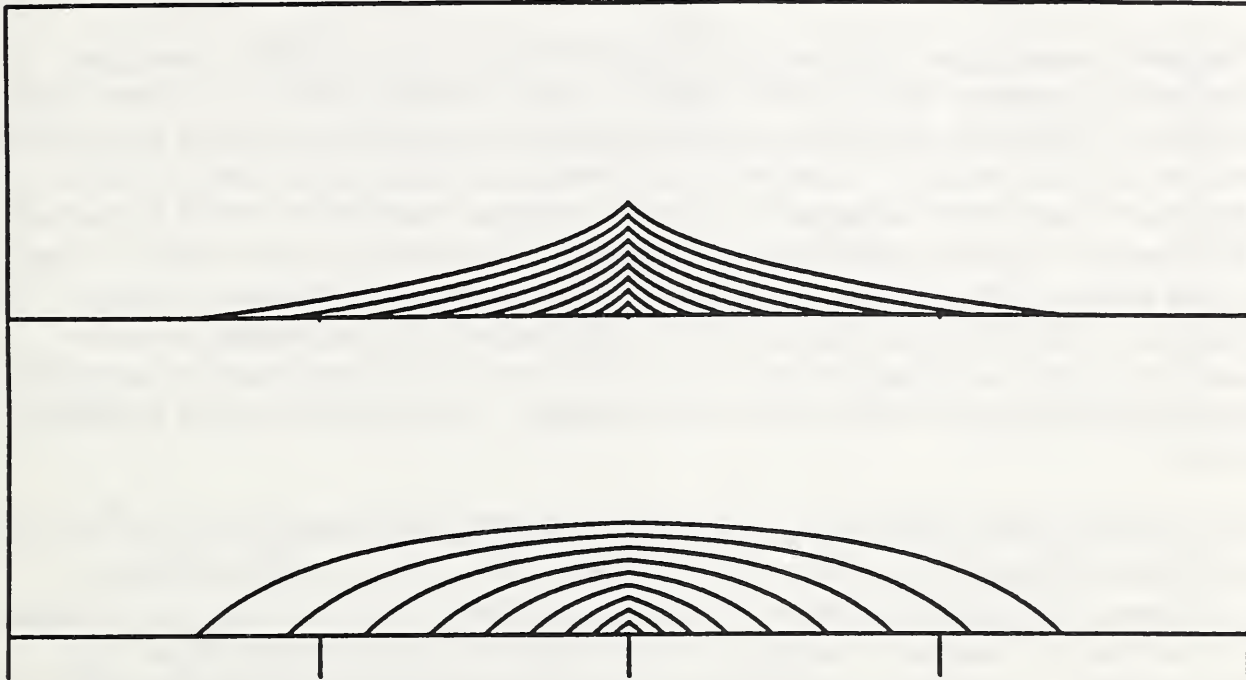


Fig. 2. Modeled evolution of the shape of a dendrite growth front. In the upper figure, it is assumed that the dendrites grow as horizontal branches from a vertical stem, while in the lower figure they grow as vertical branches from horizontal stems.

Titanium castings are important in aerospace applications, and one of the major problems of making such castings with accurate dimensions is the reaction of the molten metal with the shell mold. This causes the castings to be contaminated with oxygen to depths ranging from 20 to 2000 μm . The oxygen-rich surface layer, referred to as the alpha case, is brittle and must be removed by chemical milling. Incorporation of a model for alpha case thickness prediction into commercial casting software would allow the investment casting industry to determine how long the chemical milling process needs to be, and how much the pattern for the mold has to be enlarged to account for the material that will be removed.

The oxygen penetration into the surface region of the titanium alloy is controlled by the oxygen content at the surface of the alloy and the rate of diffusion into the metal. The former is determined by the decomposition of ZrO_2 , the major constituent of the shell mold near the metal surface. Thermodynamic calculations were used to obtain this value as a function of temperature and to predict whether the Ti is liquid, or solid with the beta or alpha crystal structure. Various diffusion models were developed and are now subject to

experimental verification in collaboration with Howmet Corporation. Howmet poured two instrumented castings of Ti-6wt%Al-4wt%V to obtain experimental temperature-time data at different points on the casting surface. The local oxygen penetration at these points is being measured to be compared to that predicted by the model for the measured thermal history. In addition, the measured temperatures are being compared to temperatures predicted by the casting modeling software. The eventual goal is to develop a system in which the alpha case thickness can be predicted from the diffusion model, using the thermal history predicted by the casting model.

Successful modeling of metal casting is dependent upon the availability of accurate thermophysical properties for all of the materials involved in the process. At present such data are not available for most of the required properties, especially at the high temperatures where they are most needed. Therefore a major project is under way to obtain accurate thermophysical and related properties on selected aerospace materials by use of millisecond- and microsecond-resolution pulse-heating techniques. The materials under study are superalloys and titanium alloys selected as being of specific interest to Consortium members. The experiments on these aerospace alloys will be supplemented by measurements on well-characterized binary and ternary alloys with the objective of developing methods to predict thermophysical properties of alloys from the knowledge of the properties of the constituent elements.

Measurements were performed on a superalloy (IN718) and a titanium alloy (Ti-6Al-4V) at temperatures ranging up to several hundred degrees above the liquidus temperature. Figure 3 shows the electrical resistivity of the titanium alloy in both the solid and the liquid state. Note that the changes in resistivity are not large: the vertical scale in figure 3 is greatly expanded. In addition, measurements were carried out on a Nb-Ti alloy to gain a better understanding of rapid melting phenomena as they apply to alloys.

All of these projects involve direct working collaborations between NIST workers and scientists at the Consortium member companies. The collaborations have made it unnecessary for NIST to develop expensive facilities for casting of superalloys or titanium, since experiments requiring such castings are much more efficiently done using the equipment and expertise of the industrial members. At the same time, NIST and the university members of the Consortium have been able to carry out longer-term projects such as model development and property measurements that would be outside of the time constraints of industrial workers concerned with immediate production problems.

Some results of the consortium work, such as thermophysical properties data, are already being used by the consortium's industrial members. Other projects, such as the solidification path analysis, will continue to develop over a period of several years, but the results are being assembled in a format that will be readily incorporated into the ProCAST software which Consortium members use to analyze the casting process. As work proceeds, projects have been reevaluated and emphasis changed. For example, a project to use an eddy current sensor to locate the solidification front was dropped after measurements showed that the

electrical properties of the alloy and the mold material at high temperature would result in inadequate sensitivity. In contrast, the x-ray sensor has shown good promise, and NIST is now investigating how it can be implemented in a furnace at Howmet.

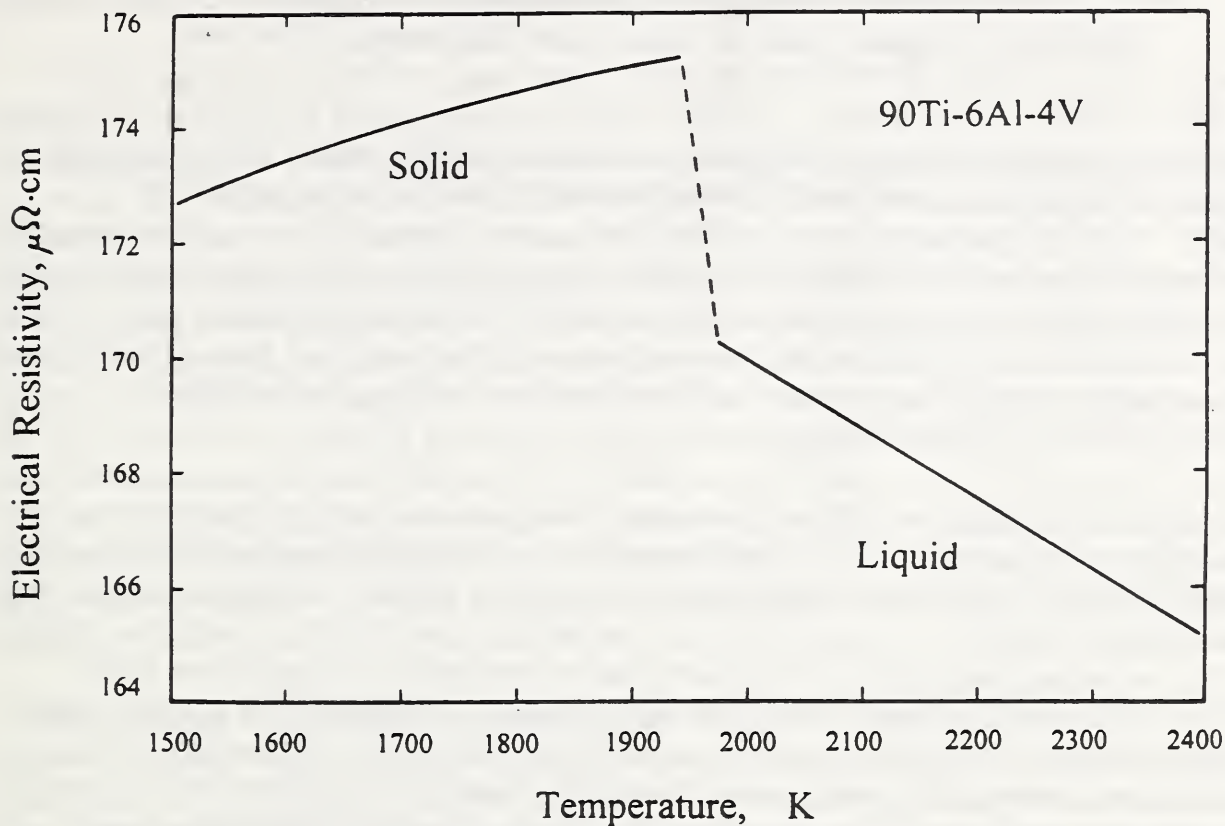


Fig. 3. Measured electrical resistivity of solid and liquid ti-6Al-4V.

In addition to the working collaborations on individual projects, the consortium holds meetings twice a year and publishes quarterly, semi-annual, and annual reports. It is anticipated that some of the results of the consortium's work will also appear in the open literature, starting next year.

PUBLICATIONS

1. Semi-Annual Report, NIST Consortium on Casting of Aerospace Alloys, October 29, 1993
2. Annual Report, NIST Consortium on Casting of Aerospace Alloys, April 25, 1994.

On-Line, Non-Destructive Magnetic/Mechanical Property Measurements in the Rolling Mill

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One of the greatest challenges facing the steel-making industry today is the consistent production of large quantities of steel with well-controlled and uniform mechanical properties. For example, approximately 65 million tons of sheet steel per year are produced in the United States, and it is estimated that, if the rejection rate of this type of steel product could be cut in half, a savings on scrap on the order of 100 million dollars per year could be realized. Further savings would result from reductions in the amount of time-consuming and costly mechanical testing now required, and from increases in the end-use efficiency available from a more uniform product.

To help steel producers to achieve the needed production and testing improvements, we are investigating on-line methods for the measurement of mechanical properties using a magnetic approach. This work is being carried out under a CRADA with the American Iron and Steel Institute (AISI). In a separate project under this same CRADA, predictive tools which link processing parameters of a hot strip mill to mechanical properties are being developed. The goal is a system that would enable rolling mill operators to quickly change processing variables, such as annealing temperature and roll pressure, when the on-line sensing equipment recognizes that the steel is deviating from specifications. We also are cooperating with the Industrial Materials Institute of Canada, who are developing laser ultrasonics for on-line measurements of acoustic attenuation, providing an additional parameter related to mechanical properties.

It is generally recognized that the mechanical properties of steel, i.e. yield strength, ultimate tensile strength, elongation, etc., are directly related to the steel's chemical composition, thermal history, and microstructure. These same parameters also affect the magnetic properties, providing the basis for relating changes in magnetic properties to changes in mechanical properties (see, for example, references 1 and 2.) However, different magnetic properties, such as the initial permeability, coercive force, resonance, Barkhausen signal, etc., respond in different ways to changes in the microstructure. For this project, a magnetic property that minimizes changes due to internal and external stresses, and maximizes changes due to yield stress, is required. Our past efforts have shown that the first moment obtained from a plot of the Barkhausen signal strength vs. applied magnetic field, herein called the jumpsum rate first moment (JSR first moment) best satisfies this requirement.

Our industrial collaborators (LTV and Wierton Steel) provided a large number of samples of four grades of steel from their production lines for this work. These were, listed in order of increasing yield strength, ultra low carbon (ULC), low carbon (LC), mid range

(MR), and high strength low alloy (HSLA). In last year's report, we presented results that established a well-defined linear relationship between the hardness of these materials and the JSR first moment. Based on our results, along with the method used to obtain the JSR first moment, AISI is filing a patent application for this method of hardness measurement.

Results during the previous year clearly indicated that the JSR first moment is a good indicator of mechanical properties on a "global" scale, i.e. when all the grades of steel are considered together. Work this year focused on establishing relationships on a "local" scale, i.e. when only a single grade of steel was considered. Extensive mechanical, metallurgical, and magnetic data were obtained on more than 40 samples of each grade of steel. The data indicate that, whenever a good relationship between hardness and a mechanical property exists, a good relationship between JSR first moment and the same mechanical property can be found. However, the sample set from only one of the grades of steel, HSLA, was adequate to obtain good magnetic/mechanical relationships. Analysis of the data indicated that the reason for the lack of good local relationships for the ULC, LC, and MR sample sets was that these samples were drawn from a wide range of heats, each heat having different chemical compositions and processing. For example, the ULC sample set contained both Ti-stabilized, batch-annealed material and Nb-Ti stabilized, continuous-annealed material, with each of the two types of material having too narrow a range of yield strengths to obtain good statistics.

To overcome the problem of obtaining good magnetic/mechanical relationships we devised a method to alter the yield strength of a sample by inducing a small amount of plastic strain. In this way, a useable range of yield strengths can be obtained from material with nearly identical composition and processing parameters. For example, Figure 1 shows the yield stress vs. JSR first moment obtained on a midrange material processed in this way. An excellent linear correlation is obtained. Figure 2 shows the relationship between JSR first moment and work hardening coefficient. Again, an excellent correlation exists.

The parameter of greatest interest to the steel producer is the yield stress. Very tight tolerance must be maintained. To be useful on-line, a measurement technique must be able to detect changes in the yield stress as small as 4 MPa (0.5 ksi). The critical parameter determining the sensitivity of the JSR first moment to changes in yield strength is the slope of the correlation line shown in Figure 1. From this slope it can be seen that to detect changes in yield strength of 4 MPa, the JSR moment will need to be measured to a precision of about 10 A/m (0.1 Oe). A precision of 1 A/m is readily achieved in the laboratory, so that, with good engineering, the 10 A/m figure should be achievable on line.

While magnetically and mechanically evaluating a large number of tensile samples made from the four grades of steel, we conducted experiments that examined the effect of Barkhausen probe location. Because the samples we received had been coiled, the upper and lower surfaces were under different stress and would give different signals at low applied stress. A special probe was developed that could detect the signal simultaneously from both sides of the sample. To obtain a composite signal for averaging the surface stresses the new

probe has the further advantage that extraneous noise tends to be canceled, whereas the random Barkhausen signals are preserved. This type of probe will be further investigated for on-line use.

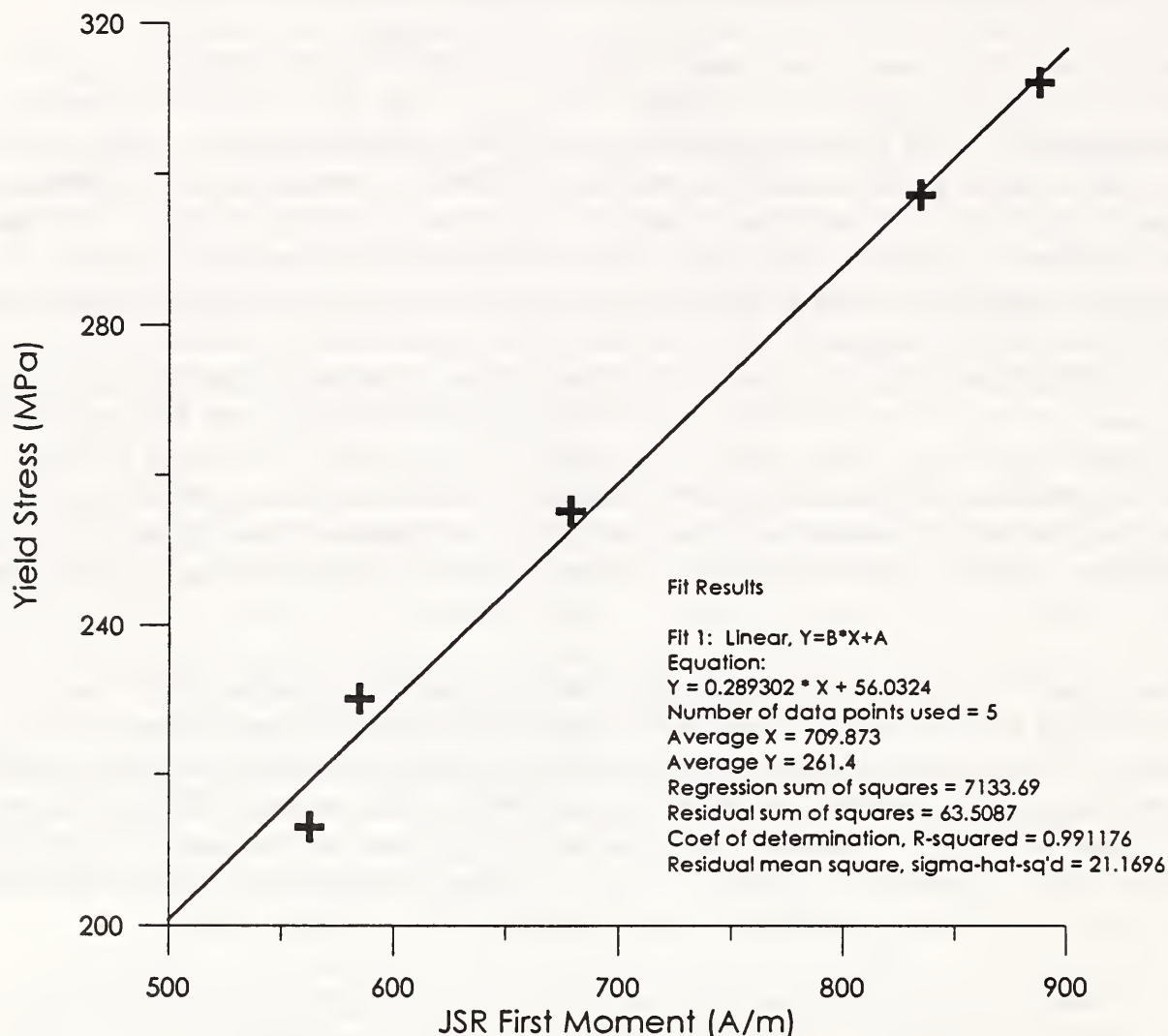


Fig. 1. The yield stress versus JSR first moment for samples of one grade (MR) of steel subjected to various degrees of plastic strain. The line is a least squares linear fit to the data.

The results of Fig. 1, though very instructive, can be criticized because the plastic strain given the samples in the laboratory was not equivalent to the strain induced by thickness reduction in a rolling mill. To better determine the needed magnetic/mechanical relationships on the different grades of steel, a more realistic experiment is being conducted. In this experiment the experimental rolling mill at LTV will be used to subject two different heats of each grade to a matrix of processing steps that are actually used to change yield stress during processing in the mill.

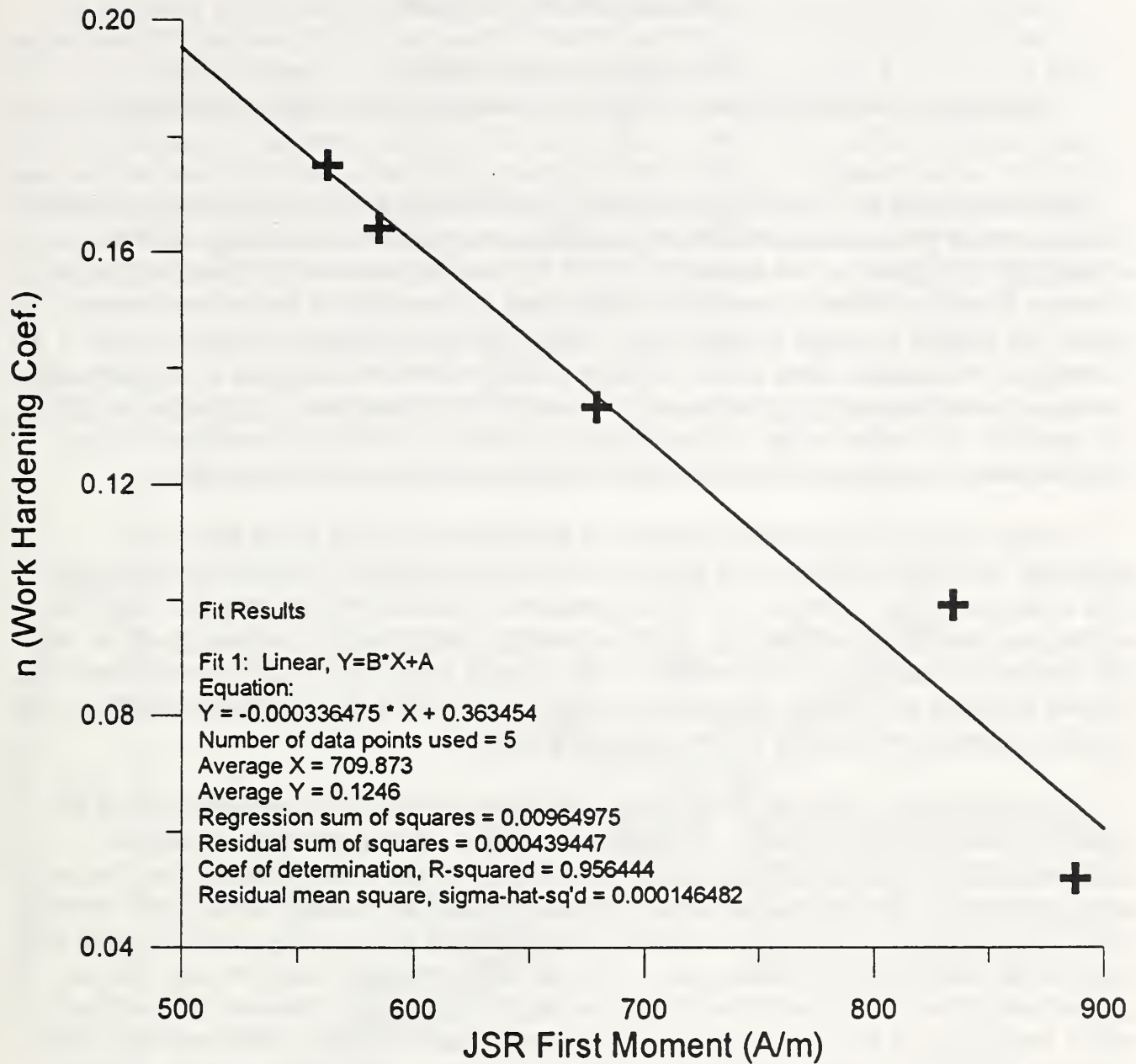


Figure 2. Work hardening coefficient versus JSR first moment for samples of one grade (MR) subjected to various degrees of plastic strain. The line is a least squares linear fit to the data.

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Modeling for Arc Welding

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The objective of this research is to develop models of arc welding processes that can be used to increase productivity and final weld quality. A model of the shielded metal arc welding (SMAW) process was developed in FY 94 in collaboration with researchers at the Colorado School of Mines to predict the temperature of the electrode away from the arc region. In SMAW a voltage is applied to a solid metal core wire and an arc is created between the wire and the base metal. The arc melts the base metal as well as the wire. A mixture of materials covers the wire, and as the covering decomposes, it provides an inert gas shield for the molten metal; the covering also is used to control the metallurgy of the solidified weld by adding alloys, deoxidizers, fluxing agents etc. to the weld pool.

During welding, the electrode increases in temperature because of the Joule heat generation within the electrode and because of the heat transferred from the arc through the melt at the end of the electrode. If the temperature of the electrode becomes too high, the coating can decompose prematurely, which adversely affects the final metallurgy of the weld and changes the melting rate and transfer mode (droplet size) [1]. The model predictions can be used to design the coating composition and/or weld schedule for a particular electrode and therefore increase productivity while maintaining quality.

The heat transfer equations of the melting electrode were solved: conduction along the electrode, Joule heat generation in the electrode, the heat of decomposition of calcium carbonate in the covering, and heat delivered to the end of the solid electrode from the melt were considered. The thermal properties of the core rod were allowed to vary with temperature. The coating was modeled as a thermal mass (constant heat capacity) with the same axial temperature distribution as the core rod. The rate of heat transfer from the melt was set proportional to the current with the constant of proportionality ψ determined by matching model predictions of the melting rate to experimental results. A finite difference technique first used in [2] was used to solve the final set of non-linear equations (a moving boundary problem).

Experiments to develop and verify the model were conducted on E7018, 354 mm long, 3.2 mm diameter, commercial electrodes at the Colorado School of Mines under the supervision of Professor Stephen Liu. Type-k Chromel-Alumel thermocouples were placed in holes of 1 mm diameter, drilled through the covering to the centerline of the rod at 25 mm intervals starting at 120 mm from the tip. Thermocouple data were recorded for currents of 110, 130, and 150 A. The melting rate was recorded for four different currents from 118 to 160 A.

By adjusting ψ , the root mean square (RMS) difference between the model and the experimentally measured consumed length of electrode (Figure 1) was minimized. For $\psi = 2.4$ V, the RMS difference was 2 mm. This compares with values of 2.8 - 5.4 for ψ found by Waszink and Piena [3], who modeled only the tip of the electrode. The temperature profile predicted by the model starts at the temperature of the holder, climbs gradually and then remains relatively flat before rising sharply to the melting temperature at the end of the electrode (Figure 2). The model-predicted temperature profile for the recommended welding current (130 A) agreed well with experimental results; for the thermocouple 270 mm back from the electrode tip there is a difference of 3% (16 °C) after 40 s of welding (Figure 3). The model over-predicts the temperature profile for welds made at 110 and 150 A. For a 150 A current, there is a difference of 34% (331 °C) at 270 mm and 40 s. For a 110 A current, there was a difference of 40% (98 °C) at 270 mm and 40 s. The 110 A and 150 A currents represent the extreme ranges of current of practical weldability for this electrode.

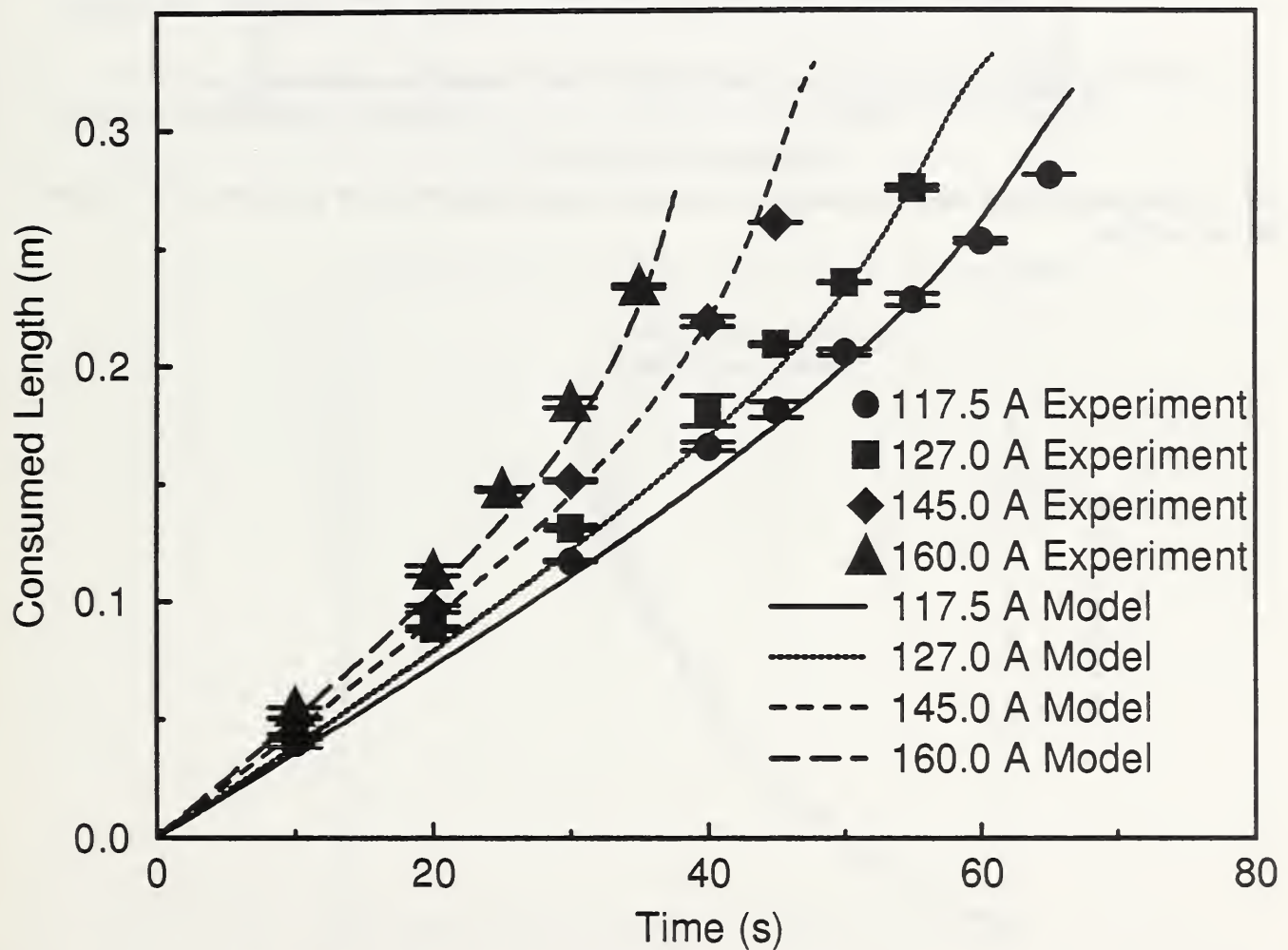


Fig. 1. The model-predicted and experimental lengths of the consumed electrode. The model predicts the consumed length to ± 2 mm.

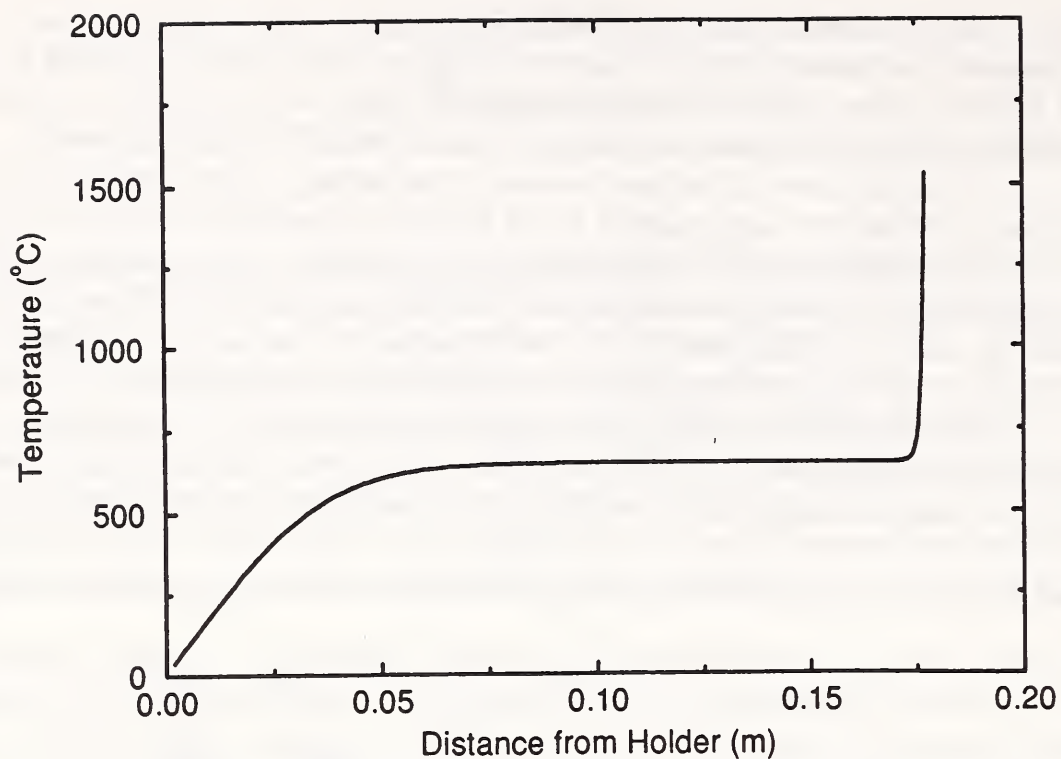


Fig. 2. The temperature profile predicted by the model along the electrode for a current of 130 A after 40 s of welding.

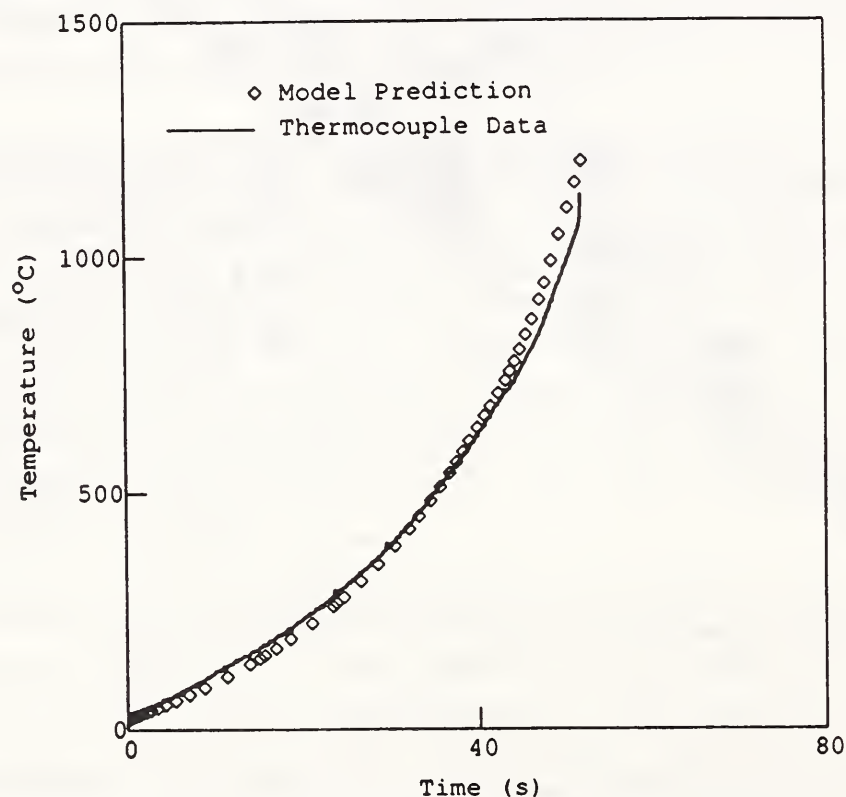


Fig. 3. The model-predicted and experimental temperature history 270 mm away from the tip of the new electrode. The electrode was welded at 130 A. The model predicts the temperature to 3% of the experimental results after 40 s of welding. For the same position and time at 110 A and 150 A, the model predicts the temperature to 40 and 34%.

In summary, a heat transfer model of the SMA electrode was developed to predict the temperature profile and melting rate. For the conditions studied, the model could predict the consumed length of the electrode to 2 mm. For the recommended welding condition (130 A), the predicted temperature profile agreed well with experiment (to 3%, 16 °C, at 270 mm from the electrode tip after 40 s of welding). The model could be used for weld schedule design or as an analysis tool in covering design. The results will be presented to industry at the American Welding Society's annual convention in April of 1995.

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Consortium on Intelligent Processing of Ceramic Powders and Slurries

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The overall goal of this project is to use electroacoustic analysis, nuclear magnetic resonance (NMR) spectroscopy and NMR imaging (NMRI), x-ray photoelectron spectroscopy (XPS), and Auger electron spectroscopy (AES) to obtain and interpret data needed for intelligent processing of sintered, reaction-bonded silicon nitride (SRBSN). The following were the specific objectives for this year: analysis of surface chemistry, surface reactions and reaction rates of powders in aqueous solvents containing polyelectrolytes and polymers; measurement of agglomerate size-distribution changes as a function of slurry bulk chemistry and aging time; determination of powder homogeneity through the characterization of surfactant distribution in slurries by NMR imaging; and characterization of the Si powder surface due to interaction with water and impurities using XPS and other spectroscopic techniques.

Reproducibility in processing is recognized as a vital component of cost-effective manufacture and improved reliability in the application of advanced ceramics. This is particularly true for sintered reaction bonded silicon nitride due to its chemical complexity. Since fine size powders are the starting materials for the production of these ceramics, their study has been the focus of this project. Preparation and dispersion of ceramic powder slips require knowledge of the particle size distribution and particle charge properties under varying conditions and at high solids concentrations. Recent advances in electroacoustic theory and instrumentation have led to the development of novel techniques for slips characterization.

The electrokinetic sonic amplitude (ESA) technique allows us to obtain information about the powder surface chemistry as a function of various parameters and in suspensions containing over 30 volume percent solids. The ESA effect is caused by a periodic displacement of the suspended particle and surrounding ion atmosphere in a MHz frequency range electric field. The magnitude of the ESA signal increases with volume fraction and density difference of the solid phase. In addition, a phase lag can occur between the applied field and the acoustic response due to particle inertia and the damping effect on dynamic mobility increases with both frequency and particle size. The frequency spectrum of the mobility and phase lag (Figure 1) provides information from which the particle charge (zeta potential) and size (mass average) can be calculated according to O'Brien's theory [1] (Figure 2). These measurements are being made on a new instrument, the Acoustosizer^(R) by Matec Applied Sciences.

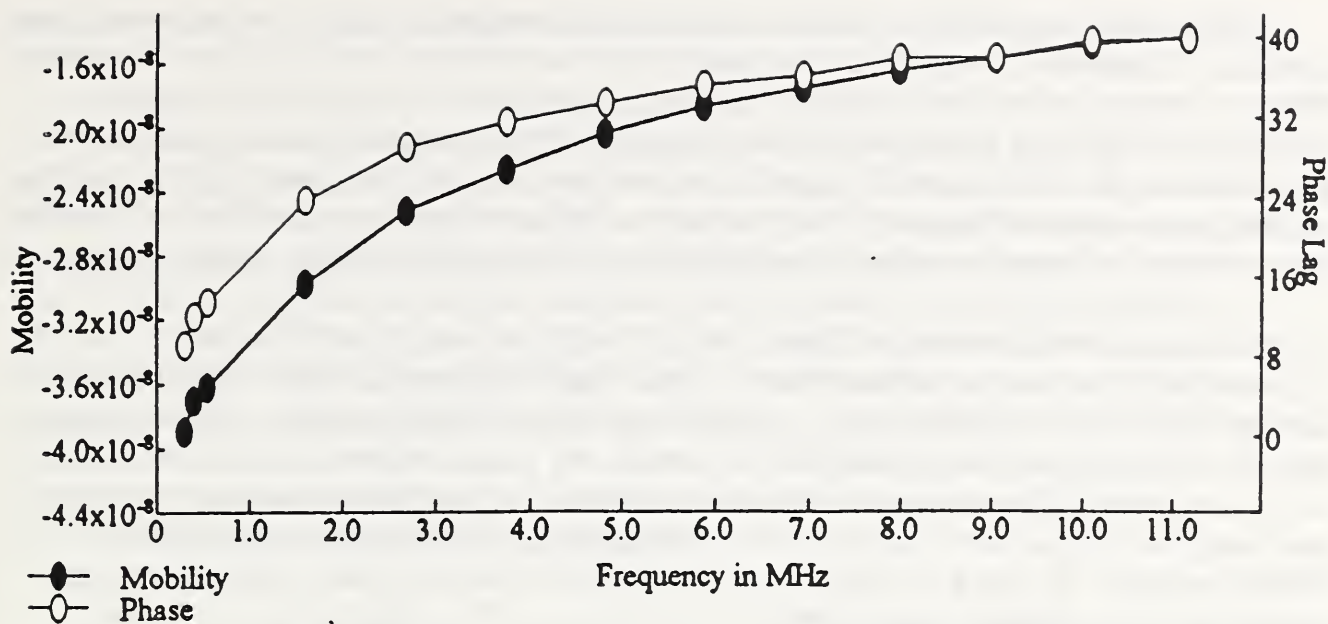


Fig. 1. Frequency spectra of dynamic mobility and phase lag for nominal 1.0 μm silica at 5 vol. % in pH 5.9 aqueous sodium nitrate solution.

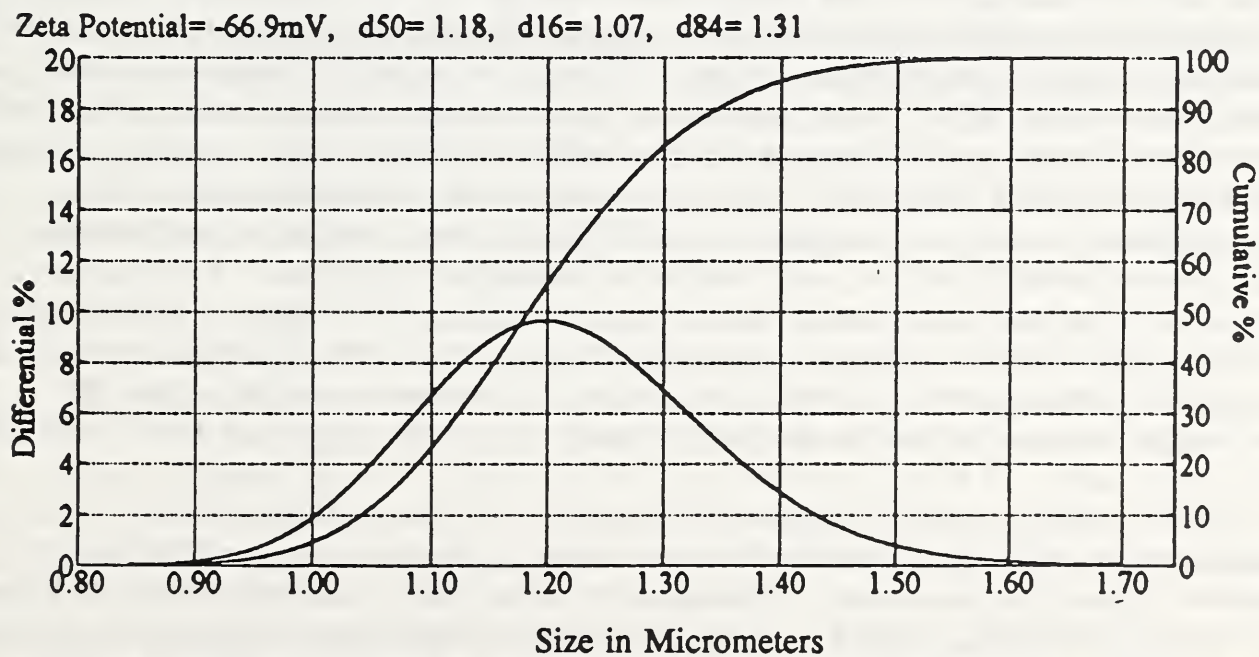


Fig. 2. Size distribution for nominal 1.0 μm silica at 5 vol. % in pH 5.9 aqueous sodium nitrate solution. A log-normal distribution function is assumed in fitting the spectral data.

NMR is used in our studies because it has the following advantages over other techniques in materials diagnosis: samples can be characterized non-destructively for different nuclei at different frequencies for their spatial distribution; samples can be characterized in-situ in several ways, e.g., not only spin densities but also different relaxation times can be measured to understand the environment of a specific nuclear spin. On the other hand, XPS and AES are surface-sensitive techniques probing the first $\sim 100\text{\AA}$ surface layer of solids, and provide the information on powder surface composition, and chemical form of the surface impurity.

A consortium was initiated in September 1993 with seven members (Golden Technologies, Cercom, St. Gobain-Norton, Matec Applied Sciences, Eaton, Kerr-McGee and the Oak Ridge National Laboratory). The primary focus of this consortium is on development of basic understanding of the SRBSN powder and slurry behavior to guide processors and measurement of a suitable parameter for adaption to on-line measurement and control. Our focus thus far has been on two of the most significant problems associated with the SRBSN process: the aging of silicon in aqueous environments and the interaction between powders in multicomponent suspensions.

Electroacoustics-- Comparative studies were performed using 5 volume percent suspensions of model silica powders to evaluate the Acoustosizer (AZR) system under well-defined conditions [2]. Particle sizes of 0.5 and 1.0 μm nominal diameter were used in the initial study. Measurements were made on well-dispersed suspensions over a pH range from 10 to 2. For comparative purposes, the powders were analyzed by several more conventional techniques including x-ray sedimentation (XRS), scanning electron microscopy (SEM), Mie light scattering (MLS), quasi-elastic light scattering (QELS), and d.c. electrophoresis. The last three techniques require highly diluted samples (50 - 150 mg/l solids); whereas, the acoustosizer can analyze moderate-to-dense suspensions (hundreds of grams per liter). Initial results show good agreement between the AZR median diameter (50 percent mass finer) and that determined by XRS for both powders and at similar solid volume fraction. This demonstrates that electroacoustic measurements are sensitive to particle mass in a manner analogous to the hydrodynamic situation of particle sedimentation in a gravitational field. MLS measurements, sensitive to a higher moment of particle size, tended to overestimate the 0.5 μm powder, probably due to a small number of undispersed aggregates. A comparison of the 15 to 85 percent mass interval indicates that the AZR is underestimating the size spread for these suspensions. A study is currently underway to model the effects of size distribution on the ESA measurement and eventually compare this to experimental data; the AZR currently assumes a log-normal distribution, which may not be appropriate for all situations.

We have also compared zeta potential values derived from dynamic mobility measurements using the AZR with those determined by the standard d.c. electrophoresis method [3] on dilute suspensions. Measurements were made as a function of pH on 0.5 μm silica in 0.01M NaNO_3 solution. Zeta potential was calculated from electrophoretic mobility using the O'Brien and White algorithm [4]. Agreement between the two techniques was excellent over the entire measured range of pH (10 to 2) and zeta values (-90 to 0 mV). Both methods indicate an isoelectric point at pH 2.0-2.3 for this material, within the range of

literature values. These data appear to validate the O'Brien theory for thin-double layer systems.

Continuing investigations of surface chemistry and interactions in the SRBSN system have included aging studies of aqueous silicon suspensions. This work has demonstrated the unstable nature of silicon powders in this environment, and the need to control aging effects during processing. Experiments in which the ESA response was monitored as a function of time and pH showed that the surface charge of silicon powders becomes increasingly negative with time. Its surface chemistry resembles that of silicon oxide, with an isoelectric point near pH 1.5. The silicon hydrolysis reaction is accelerated under alkaline pH conditions which facilitate dissolution of oxide from the silicon surface. The ESA magnitude increases almost linearly with time at pH 10. Below pH 8 no significant change occurs in the ESA response over a 20 h period, indicating that silicon can be stabilized electrochemically at neutral and acidic pH values.

Electroacoustics Modeling-- The electroacoustic response of a sphere is described by O'Brien's frequency-dependent mobility function, $G(a^2\omega/\nu)$, where a is the radius of the sphere, ω is the angular frequency and ν is the kinematic viscosity of the liquid. In practice, one encounters a distribution of particle radii so that the observed response is an average over that distribution. The modelling effort has been directed to the examination of how different size distributions influence the response. A set of Fortran codes have been written to evaluate and display the modulus and phase of the effective response for a log-normal distribution of sphere radii. These codes will be used to determine the sensitivity of the response to bimodal distributions of sphere sizes.

NMR-- As-received Elkem HQ silicon powders were characterized by NMR and XPS. The powder was found to contain a trace of silicon hydride as detected by proton NMR at 400 MHz. An interaction between the powder surface and water also was observed when the powder was mixed. A line broadening in the water hydrogen NMR signal indicated the adsorption of water molecules on the surface of Si particles. ^{29}Si NMR study showed a weak yet detectable Si signal in the slurry suggesting that a small amount of Si had been dissolved.

A new NMR imaging technique, that is different from our nuclear spin-spin relaxation time (T_2) contrast imaging for solid imaging, is being developed for powder distribution in slurries. It utilizes nuclear spin-crystal lattice relaxation time (T_1) to contrast nuclear spins and is more useful in mapping slurries. A set of data was developed for proton in water in a slurry system containing 30 wt.% silicon and 350 ppm Darvan C at pH 9.1. The value of T_1 calculated from this set of data is 2.3 s. These data are required for developing T_1 weighted imaging. In addition, we are studying ^{35}Cl and ^{14}N NMR to examine the dissociation kinetics in water of the dimethylamine-epichlorohydrin copolymer, a polyelectrolyte used as a dispersant. The study of interactions between this dispersant and powder surface is in progress by using ^{14}N relaxation.

XPS-- The overall XPS spectrum from this powder using Mg K α irradiation at 1253.6 eV showed clearly O 1s, C 1s, Si 2s, Si 2p, and O 2s XPS signals as well as a Bremsstrahlung-excited Si KLL Auger electron signal around the kinetic energy 1608-1617 eV. High resolution Si KLL scan indicated that the 1608-1617 eV peak consisted of two signals from Si and Si-O. Combined with C 1s and O 1s results, it was concluded that this powder had carbon and silicon oxide as surface impurities. It was not possible to remove the surface carbon by mixing the powder with water up to 11 days. Only a small portion of C was removed; however, the thickness of surface oxide film increased. Silicon powder surface nitridation was studied near 1000 °C by both XPS and Auger electron spectroscopy. Almost all literature reported works have been performed on crystals for semiconductor applications, and none for powders.

Overall, we have made considerable progress in this project and the consortium participants have expressed their satisfaction with the information. Future studies in the characterization of the SRBSN system include stabilization of SRBSN powders in acid and neutral pH slurries; T₁ weighted imaging of slurries; and surface oxidation of Si powder.

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Nuclear Magnetic Resonance (NMR) Studies of Organic Binders and Characteristics of Powders in Injection Molding

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Two main objectives of this project are: (1) application of nuclear magnetic resonance (NMR) spectroscopy and imaging for powder injection molding to enhance the understanding of binder effects in the molding and debinding processes; (2) development of physical and surface chemical characterization methods used for injection molding (IM) of ceramic powders by delineation of interrelationships between powder characteristics and the resulting ceramic properties in green and sintered state.

Traditional injection molding in which 15 to 35% of the void volume in powder compacts filled with organic binders is continuing to be an important unit operation to prepare green ceramics of small and complex shapes. Several issues remain to be addressed to enhance the use of injection molding. Some of these issues are related to determination of powder characteristics that affect green and sintered densities, and binder composition, distribution, and removal. In this study, we are addressing two aspects: determination of powder characteristics (physical and surface chemical) that affect molding characteristics; and homogeneity of binder distribution during green forming. During the current year, we had focused primarily on the binder distribution related issues.

This project is carried out largely through interactions with the Pennsylvania State University (PSU)-industry consortium on powder injection molding. The specific task during this period was to address binder homogeneity using the NMR technique to enable the PSU consortium to define favorable parameters for binder melting, powder mixing, processing, and molding unit operations.

Organic binders used in ceramic powder injection molding were evaluated by proton nuclear magnetic resonance (^1H NMR) at 400 MHz. Both pure binder components and the binder in green injection molded alumina compacts were studied. The nuclear spin-spin relaxation times (T_2) of protons in the binder components (paraffin wax, polypropylene, and stearic acid) were measured to allow the comparison with those in the injection molded green compacts. The T_2 for paraffin wax and polypropylene were in the 30 to 33 μs range and their intensity decay behaviors were very similar. However, the T_2 value for stearic acid was only 17 μs and its echo signal intensity decays more rapidly than those for paraffin wax and polypropylene. These data will form the basis for T_2 -weighted imaging.

Binder content variation was detected in three injection molded green compacts obtained from the same nominal blend composition. Analysis of the molded compacts also showed the presence of a specie with a T_2 value near 300 μs . This specie may be the result of reaction during processing or the presence of moisture. The width of RF-pulses used to

measure echoes did not have a significant effect on the relaxation times but should be considered in the calculation of echo intensities at equilibrium and hence the binder composition.

These alumina green compacts containing polypropylene, wax, and stearic acid also were studied for determination of binder distribution by ^1H NMR imaging. The solid imaging technique of nuclear spin-spin relaxation time (T_2) weighted imaging at 400.159972 MHz was used for this study. The imaging technique utilizes a multiple pulse sequence for echo detection and phase encoding. Two- and three-dimensional images were constructed from the intensities of these nuclear echo signals. The spatially-resolved two-dimensional images obtained by the application of this technique indicated that the green compacts fabricated from the same nominal binder composition did not have the same composition as expected. This observation agrees well with our conclusion drawn from nuclear spin echo studies by Hahn's pulse sequence. A 64x64x64 slice in three-dimensional imaging revealed that the binder distribution inhomogeneity, and therefore, internal imperfections exist at certain parts of the samples. A binder-rich folding line was also detected in one of these green compacts.

Organic binders used in ceramic powder injection molding were molded in various compositions and evaluated by proton nuclear magnetic resonance (^1H NMR) at 400 MHz. The molding parameters were identical to those used for alumina green compacts studied last year so that processing effects can be tested for a simpler system (binder only, no ceramic powders). The samples were molded with different ratio of polypropylene glycol/wax/stearic acid. The solid imaging technique of nuclear spin-spin relaxation time (T_2) weighted imaging at 400.159972 MHz was used. The imaging technique utilizes a multiple pulse sequence for echo detection and phase encoding. 64x64x64 three-dimensional images were constructed from the intensities of these nuclear echo signals. These images revealed the presence of binder distribution inhomogeneity and a binder-rich "skin", indicating that processing of binders alone appears to produce defects.

Besides T_2 -weighted imaging of molded binders, we also studied nuclear spin-crystal lattice relaxation of stearic acid. The stearic acid is widely used in injection molding as a debinding aid. Our previous T_2 study of stearic acid found a mobile proton species of unknown origin. We measured nuclear spin-crystal lattice relaxation time (T_1) of 6.48 s by T_1 IR (T_1 inversion-recovery) method.

The sample was heated to 40, 55, 65, 70, 80, and 90 °C to create a new crystal environment and then cooled back to room temperature for T_1 measurements. It was found that T_1 decreases as a function of temperature until its melting point, 70 °C. This irreversibility concludes that as stearic acid molecular dynamic increases by thermal energy, crystal site changes to favor the molecular motion. This site remains as it was cooled to room temperature, as it was in our ceramic green compacts after injection molding at high temperature. This new, free molecular site may provide a better structure for the debinding process.

These results will be communicated to the PSU consortium to be incorporated into their program on optimization of injection molding parameters. Based on their results, a new set of samples will be produced for our studies. Some of this research will be extended to water based injection molding of silicon nitride powders.

Fluorescence Spectroscopy and Optical Monitoring of Polymer Processing

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The goal of this program is to develop optical-based sensor technology to measure, nondestructively and in real-time, polymer processing parameters. The sensor technology is based primarily on fluorescence spectroscopy and is designed to monitor rheology and temperature of polymer resins during processing.

The program is being carried out in a consortium with members of the polymer processing industry. Consortium members are 3M Co., DOW Chemical Co., DuPont Co., Rohm and Haas Co., and Dynisco. The consortium program was initiated in June 1992 after workshops and other meetings with potential industrial partners. The current phase of this program will end in June 1996.

Fluorescence spectroscopy and optical fiber cables, which are inserted into process equipment using existing instrumentation ports, are the main tools used to attain our measurement objectives. Temperature-sensitive fluorescent dyes that are doped into the polymer resin at parts per million concentration are used to acquire resin temperature. This method of measuring temperature is superior to using thermocouples because the thermocouple measurement yields the temperature of the processing machine, not that of the resin. For polymer rheology observations, orientation-sensitive dyes, i.e. dyes with large geometric anisotropy, are used to make fluorescence anisotropy measurements that give information about stress applied during processing and about orientation of the polymer matrix at the molecular level. Another rheological parameter, strain rate, is measured using photobleachable dyes; the fluorescence of these dyes is neutralized by ultraviolet light and, upon removal of UV light, the strain rate is obtained from the rate of fluorescence recovery.

The purpose of fluorescence anisotropy measurements in processing is two-fold: to characterize molecular orientation of the polymer product; and to measure the stress applied to the resin undergoing flow. We have used fluorescence anisotropy of dyes doped into polymer melts to monitor stress-induced molecular orientation of a polymer matrix undergoing flow. Both shear flow and extensional flow were studied [1,2]. We observed that, under conditions of shear flow, fluorescence anisotropy of fluorescent dyes that were covalently tagged to the polymer molecule decreased with increasing shear stress. Under extension, however, anisotropy increased with stress. A mathematical model which expresses anisotropy as a function of orientation factors of the fluorescent dye was developed to describe this behavior. The model demonstrates that the combination of dye orientation factors contributing to fluorescence anisotropy upon application of shear stress is different from those which are effected during extension. Polymer products that are processed by extrusion undergo stresses at the exit die that establishes shape and size of the product. The

stresses, of course, produce molecular orientation and their real-time monitoring is a quality check on the process.

Fluorescence anisotropy can also be used to measure the stress applied to a resin in flow via the orientation that is produced by the stress. The relationship between fluorescence anisotropy and stress is described by the stress-anisotropy coefficient that is obtained through a series of calibration measurements. Ultimately, our objective is to use real-time anisotropy measurements to monitor stress during processing by calculating the applied stress from the stress-anisotropy coefficient. In order to obtain a full rheological description of resin flow, the stress to strain rate ratio, which is the viscosity factor, is needed by the processor. Thus, an additional sensor requirement, which we are pursuing in the current year, is the development of a strain rate sensor based on fluorescence techniques.

An optical sensor that uses polarizing optics was designed, constructed and successfully used to obtain real-time measurements of fluorescence anisotropy during extrusion of polycarbonate doped with perylene. The sensor was inserted into a slit die rheometer mounted at the exit of the extruder and used to measure anisotropy as a function of shear stress. From ongoing experiments, we will obtain stress-anisotropy coefficients as a function of temperature and resin composition.

In some cases, it is desirable to tag the fluorescent moiety to the main chain of the polymer in order to obtain information about molecular orientation. Pyrene tagged poly(methyl methacrylate) was synthesized for measurement of the production of excimer radiation from overlapping pyrene rings as a function of applied stress. This approach is an alternative to the fluorescence anisotropy method for measuring stress.

The development of instrumentation to monitor resin temperature during extrusion has been emphasized during the past year. Shear heating of extruded resins is a prominent problem because resin temperature can rise above the degradation temperature and because flow properties depend strongly on temperature. For this measurement, an optical fiber sensor consisting of a bundle of optical fibers was inserted into a standard instrumentation port on the extruder. We monitored temperature by measuring the excimer fluorescence radiation from the temperature-sensitive dye, bis(-pyrene) propane, doped into poly(methyl methacrylate). Shear heating was effected by increasing the extruder screw rpm. In addition to the optical fiber sensor, an IR radiometer and a thermocouple were positioned in standard 1/2 inch instrumentation ports at the same position on the extruder line. Both fluorescence and IR radiometer temperatures increased by more than 10 °C upon change from 20 to 40 rpm, but the thermocouple temperature rose only by 2 °C, verifying that the thermocouple monitors the machine temperature and yields only small changes in temperature because of the large thermal mass of the machine.

Shear heating during extrusion also produces large temperature gradients and overshoots above the machine temperature set point. The possibility of using temperature-sensitive dyes to measure temperature profiles non-destructively has been the focus of model calculations.

The results of these calculations demonstrate that the technique which employs confocal optics is capable of temperature and spatial resolutions of 1 °C and 1.5 mm respectively using bis(-pyrene) propane. The confocal optics approach consists of focusing the excitation light for fluorescence to a point in the resin and using a pin-hole aperture at the detector to select the fluorescence from the point of focus. Fluorescence created at positions off the point of focus is prevented from entering the detector by the pin-hole aperture. Laboratory experiments to demonstrate the confocal optics design are underway.

Previous work involved the development of an optical sensor to monitor polymer injection molding [3,4]. The sensor consists of an optical fiber that is inserted through the mold wall and is positioned to view the resin in the mold cavity. It is a multi-functional device that can be used to monitor mold filling, temperature, polymer solidification, and product shrinkage. The measurement of temperature and the detection of the glass transition temperature in glassforming polymers require that a temperature sensitive fluorescent dye be doped into the resin at low concentrations. Mold filling, polymer crystallization, and product shrinkage can be detected using light reflections from the resin and do not require a fluorescent dye. The shrinkage detection utilizes an interferometer geometry of the optical sensor to measure separation and motion of the molded product away from the mold wall.

We have been developing models to describe the behavior of an injection molding fiber optic sensor [5,6]. The sensor was used for excitation light transmission and fluorescence measurements during injection molding of polyethylene, polypropylene, and polystyrene. The data were analyzed by constructing a model of light transmission and fluorescence detection in crystallizing and glass-forming resins. The calculations yield information about the time of crystallization and glass formation, the thermal resistance at the resin/mold interface, and volume relaxation in a rapidly cooled glass-forming resin. During the past year, a patent was awarded for this new sensor technology [7].

In the case of injection molding of polyethylene, a temperature-sensitive dye, dimethylamino diphenylhexatriene, was used to detect crystallization by measuring the effect of heat generated during crystallization. The dye, which is excluded from growing microcrystals, occupies neighboring amorphous regions that increase in temperature upon crystallization. To model the behavior of the optical fiber sensor and the detection of fluorescence in real-time, we take into account the absorption of excitation light, temperature functionality of the dye, multiple light scattering by microcrystals, optical geometrical correction factors, and the thermal resistance at the resin and mold interface. Figure 1 shows calculated and measured fluorescence intensity versus time where $t = 0$ corresponds to the time of mold filling. The mold at 25 °C is filled with polymer melt at 200 °C in a fraction of a second. Upon cooling, fluorescence intensity increases, but its monotonic ascent is momentarily interrupted at $t \approx 18$ s; this is the effect of the heat of crystallization and the calculations show that this short plateau in the observed data at $t \approx 18 - 20$ s coincides with the completion of crystallization. At long times, fluorescence intensity levels off as the resin approaches ambient temperature.

The emphasis of the current year's effort was in three areas: the measurement of stress-anisotropy coefficients using an instrumented extrusion slit die rheometer, the development of the temperature profile sensor based on confocal optics, and the development of a strain rate sensor using photobleachable fluorescent dyes.

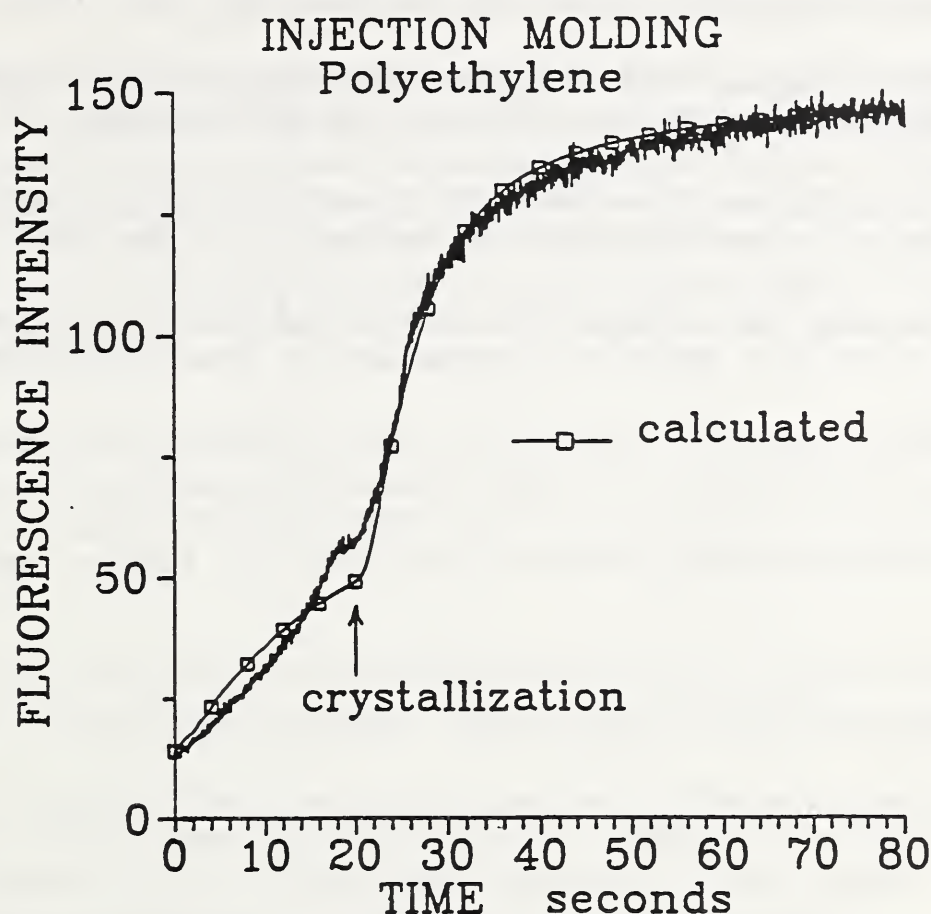


Fig. 1. Calculated and measured fluorescence intensity versus time for dimethylamino diphenylhexatriene doped into polyethylene. At $t = 0$, the mold was filled with polymer resin. The short plateau in the measurement at $t \approx 18$ s occurred at the completion of crystallization. The calculated intensity was obtained from a model that was developed to describe the behavior of the optical sensor.

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NIST-Industry Consortium on Polymer Blends Processing

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The objective of this project is to understand the variables controlling the mixing/demixing kinetics in polymer blends/alloys processes designed to tailor properties through control of the structure and morphology of the final materials. The results obtained from laboratory studies and on-line characterization techniques developed during these laboratory studies will be tested on the bench- and pilot-scale processing machine (i.e. extruder/mixer). All resulting information and technology are shared with the industrial partners of the consortium. Further process control development will be done jointly with industrial partners.

Improved process control is crucial in the manufacture of plastic products. Stringent requirements in properties and dimensional stability for new applications and in new product development, together with the complex nature of multi-phase processing in polymer blends/alloys, demand a more scientifically disciplined approach in process design and control [1].

Research in this program, conducted jointly with industry, takes this more science-based approach to process design and control. Specific topics focused in this project include:

- Phase separation behavior of polymer blends with diblock copolymer as compatibilizer.
- Construction of a shear light scattering/optical microscope instrument and study of the mixing/demixing kinetics and structure formation of polymer blends.
- Technology dissemination through the NIST/industry consortium

In the study of the influences of compatibilizer on phase separation behavior, small angle neutron scattering (SANS) and time-resolved light scattering (TRLS) measurements were carried out. SANS measurements were used to investigate the effect of polystyrene- d_8 /polybutadiene diblock copolymer (PSD-PB) content on the phase behavior of a low-molecular-weight polystyrene- d_8 /polybutadiene (PS/PB) mixture. SANS results include general features of the scattering curves as a function of temperature and copolymer content. For intermediate to high copolymer content (greater than 20 wt%), a pronounced peak in the scattering curve is observed at all temperatures. The peak intensity, $S(q^*)$, increases as temperature decreases for all samples, but the peak position, q^* , increases with increasing copolymer content and is weakly dependent on temperature. These results indicate that an ordered structure with dimension $1/q^*$ exists. A detailed analysis of the temperature and composition dependence of the peak intensity and peak position, which is a measure of the structure, is being carried out.

The phase-separation kinetics and morphology of PS- d_8 and PB upon addition of PSD-PB diblock copolymer were also studied using temperature-jump light scattering (TJLS) and phase-contrast light microscopy techniques. Upon addition of a small amount of diblock copolymer (3%), the rate of phase separation was significantly slower and the phase boundary shifted to a lower temperature by about 5 °C. These results are expected based on other systems described in the literature and the propensity of the block copolymer to concentrate at the interface, which effectively reduces the interfacial tension between the demixed phases. The light microscope is unable to resolve the early stages of phase separation in the 75/25 "critical" blend, because the size scale is smaller than the resolution of the optical microscope. Off-critical blends are easily observed; the addition of block copolymer to a 70/30 blend was examined in detail. The morphology formed in the two-phase region was smaller in size as block copolymer was added, and observations could be made up to about 5% block copolymer before the resolution limit of the light microscope was reached. Further studies using transmission electron microscopy, which has much higher resolution, are in progress. In addition we plan to do small-angle neutron scattering (SANS) experiments. A theory of blend stability upon addition of either an asymmetric or symmetric diblock copolymer was also developed in parallel to the experimental work. This system was chosen by the Polymer Blends Consortium as a model system, and an update of the work was presented to the consortium.

In the mixing/demixing study, shear light scattering measurements were carried out for a polystyrene (PS) and polybutadiene (PB) blend (50:50 by weight) dissolved in dioctyl phthalate (DOP) (8% total polymer by weight). This blend was subjected to a two-step shear quench with a delay time between the two shear rates to examine the phase separation kinetics by light scattering. In these experiments, the sample was allowed to reach a steady state at high shear rate, then "shear-quenched" to a lower shear rate. A delay time, t_d , was employed between the two shear rates in order to control the amount of structural development before the second shear rate, $\dot{\gamma}_2$, was applied. By controlling the structure evolution before application of $\dot{\gamma}_2$, the hypothesis that the existing structure affects the coarsening kinetics after cessation of $\dot{\gamma}_2$ was tested.

Three conclusions may be drawn from this study. (1) The slow relaxation of anisotropic scattering patterns produced by low shear rates to an isotropic pattern was independent of the sample history prior to the deformation. Pre-existing structure in the sample is therefore not responsible for the slow relaxation behavior. (2) The two-step experiments revealed that coarsening accelerates during application of the second shear rate, then decelerates after cessation of the second shear rate. (3) The coarsening behavior in the directions parallel and normal to flow are coupled. When phase separation occurs normal to flow during $\dot{\gamma}_2$, phase separation parallel to flow only occurs in a q -independent fashion after cessation of $\dot{\gamma}_2$. Spinodal-like phase separation parallel to flow is only observed when the second shear rate suppresses growth in all directions.

The importance of these experiments to polymer blend processing is to understand the effect of pre-existing morphology on processing and the redevelopment of morphology after

processing. The results showed that pre-existing states do not control phase separation kinetics; instead, only the processing shear rate controls the final coarsening behavior. Accelerated coarsening was observed during the second shear rate and decelerated coarsening was observed after the second shear rate. It appears that a greater extent of mixing occurs normal to the flow direction. Further confirmation by SANS measurements is planned.

A new instrument was constructed that combines some of the technology of the shear light scattering instrument described above with an additional phase contrast microscope. The resulting instrument records both the light scattering images of polymers under shear as well as the microscopic images of the polymers under flow in real space. This is an important advance in our capabilities for studying polymer behavior under shear.

A set of real (light microscope) images together with the LS patterns at the corresponding shear rates are displayed in Figure 1 to demonstrate the shear mixing of phase separate droplets (at quiescent $\dot{\gamma}=0 \text{ s}^{-1}$) to deformed domains ($\dot{\gamma}=0.2 \text{ s}^{-1}$), followed by formation of the string phase ($\dot{\gamma}=50 \text{ s}^{-1}$) and eventual homogenization at very high shear rate ($\dot{\gamma}=1000 \text{ s}^{-1}$). All these studies were carried out either with the participation or knowledge of our industrial consortium members.

A new compact LS/microscopy detection system will be built to fit on the exit port of the extruder/mixer for on-line structure characterization. Further development for on-line control will be pursued jointly with industrial partners.

This has become the key issue in gaining competitiveness in the 1990s. Although the growth in total annual production and in new product development remained strong in the late 1980s and early 1990s for polymer blends/alloys (annual growth rate of 8-10%, and a total world market of 24 billion pounds for 1994, according to the prediction by Chemical week, May 1990), the challenge of responding to specific customer/market needs while reducing the new-product development cycle can only be met through a more scientific and systematic approach, instead of the trial-and-error approach mostly used in the 1980s (see *Plastics Technology*, June 1992).

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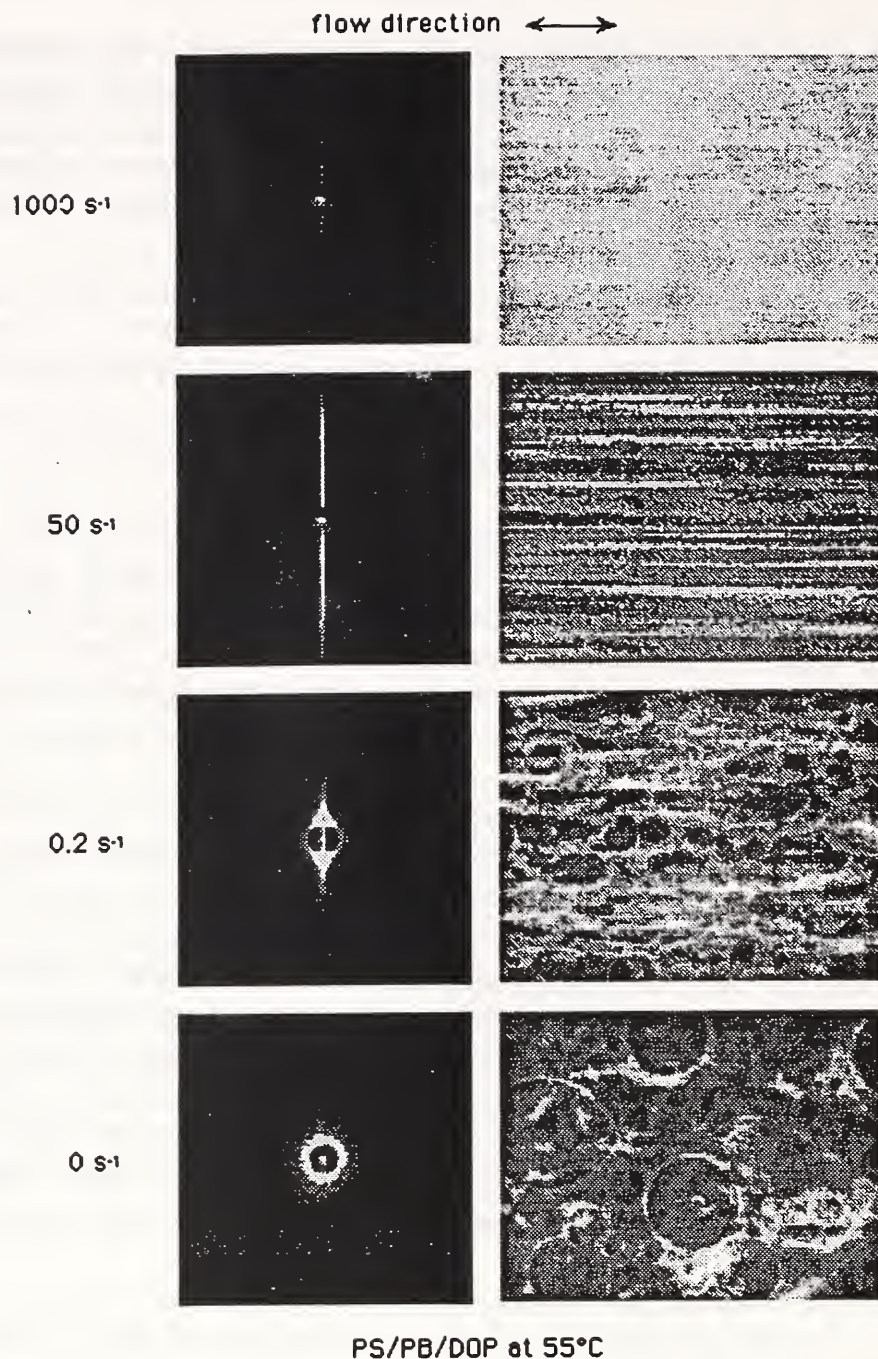


Fig. 1. A phase separated polystyrene/polybutadiene blend diluted by dioctylphthalate is subjected to different shear rates. On the left-hand side, four frames of light scattering patterns from this blend at 4 different shear rate (0 s^{-1} , 0.2 s^{-1} , 50 s^{-1} and 1000 s^{-1}) are displayed. The center spot is the beam stop; the laser light beam is sent in parallel to the shear gradient direction in this cone-and-plate rheometer. The vertical projection of the scattering pattern is the vorticity direction and the horizontal direction is the flow direction. The detector covers about 30 degrees of scattering angle in this geometry. On the right-hand side, four frames of the phase contrast microscope images of the corresponding experimental conditions are displayed. The change from phase separated domains at 0 s^{-1} to deformed domain structure at 0.2 s^{-1} , to string phase structure at 50 s^{-1} , and to almost homogenized mixture at 1000 s^{-1} can be clearly observed. The microscope image covers $100 \mu\text{m}$ by $140 \mu\text{m}$ with resolution about $1 \mu\text{m}$. However, the light scattering pattern covers in reciprocal space from $1 \mu\text{m}^{-1}$ to $10 \mu\text{m}^{-1}$, which is complementary to the real space microscope images.

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Ultrasonic Evaluation of Ceramic Grinding Damage

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The purpose of this program is to evaluate the applicability of ultrasonic techniques to nondestructively assess near-surface damage in surface-ground ceramics. Ultrasonic pulsed-wave techniques are used to evaluate the material surface and subsurface structure, with an emphasis on detecting distributed damage as opposed to discrete or individual defects. Previous researchers using acoustic microscopes at high ultrasonic frequencies (> 100 MHz) demonstrated that it is possible to detect individual damage sites in ground ceramics [1]. These techniques, however, are not feasible for use in a grinding operation. For our application, an ultimate goal is to implement sensor-based techniques in a process-control environment, for example, to monitor material removal rates. As such we restricted our work to lower-frequency transducers (< 100 MHz) that would be appropriate for this type of environment.

Motivation for this research originates from the ceramic manufacturing community's critical interest in its product quality. The brittle nature of ceramic materials makes manufacture of damage-free products difficult. Grinding-damage sites contribute to crack initiation and their subsequent growth under service stress. The depth of damage, typically on the order of the material grain size in finish-grinding, may be confined to only the top few micrometers of the surface. The surface topography, however, may be of the same order of magnitude and acts to obscure the effects of subsurface microcracking on the signature of the ultrasonic echo [2]. We previously reported on the effects and measurements of surface roughness using ultrasound [3], and on the capability of ultrasound to detect controlled subsurface cracks in silicon nitride (Si_3N_4) and glass [4]. The work reported here specifically addresses the need to distinguish the effects of near-surface damage from surface topography.

The experimental ultrasonic system consisted of a broadband pulser/ receiver, a peak-amplitude detector, and focused transducers operating with peak frequencies of 30 and 50 MHz. The samples were immersed in a water tank for convenient scanning of their flat surfaces. The transducers were attached to a scanning stage having multiple degrees of freedom (X, Y, Z, Θ , Φ) which allowed for motorized linear and raster scans under PC control. Echo-amplitude scans were made using short ($< 0.1 \mu\text{s}$) ultrasonic pulses at normal incidence to the sample surfaces. This approach for an ultrasonic evaluation of the material condition was predicated on the assumption that the echo-amplitude will be reduced by near-surface damage due to one or more of the following mechanisms: (1) increased material compliance due to shallow horizontal and vertical cracks; (2) phase interference between the surface reflections and subsurface reflections and diffracted waves; and (3) scattering by cracks of the incident ultrasonic wave away from the receiving transducer aperture.

Ultrasonic tests were performed on a number of different glass and ceramic samples. Here we report the results on two particular material sample sets consisting of "black glass" and Si_3N_4 samples. The use of high quality glass samples was considered relevant to this ceramics evaluation program for several reasons. Glass of this type is free of inherent defects, is homogeneous and isotropic, and can be well characterized. Similar machining and polishing techniques for ceramics may be used, and the materials exhibit similar grinding damage morphologies. The surface roughness may be distinguished from subsurface damage by optical means, and the roughness can even be removed while retaining the subsurface damage. These last features in particular allow us to isolate and study the effects of subsurface damage in ways that are not easily accomplished with advanced ceramic materials.

The particular black ($\approx 10\%$ iron oxide) glass samples used here were developed and characterized by other researchers [5] as candidates for neutral-density-filter standard reference materials. Three specific samples were chosen to represent a range of grinding conditions with an expectant corresponding range of subsurface damage. They were ground with respective grit sizes of 3, 9, and $22.5\ \mu\text{m}$, and subsequently lap-polished with a $1\ \mu\text{m}$ diamond grit for 24 hours. After polishing, the average surface roughness values of all three samples were much less than that of a $0.06\ \mu\text{m}$ average roughness (R_a) reference sample, thereby providing an effectively smooth topography for the echo-amplitude measurements made at the ultrasonic wavelengths ($\geq 30\ \mu\text{m}$) used here.

Ultrasonic C-Scans, where the echo amplitude at each position was measured and recorded, were made using a frequency of 50 MHz and an insonified spot diameter of approximately $60\ \mu\text{m}$. The resulting plots (not shown) of echo amplitude as a function of position did not reveal any obvious difference between the three samples. In addition, the resulting averages and standard deviations for each sample were the same, within experimental error and repeatability. However, a histogram analysis of the echo amplitudes revealed significant differences. For each sample, an amplitude distribution plot was made by sorting the individual measured echo amplitudes into bins of 10 mV width. The number of occurrences (counts) within each 10 mV-wide bin was then counted and graphed. Figure 1, showing the echo amplitude distribution for each of these samples, illustrates those differences for the three grinding-grit sizes. We are led to conjecture, based on the assumption of "ultrasonically smooth" surfaces, that we are detecting different levels of distributed near-surface/subsurface damage.

The Si_3N_4 ceramic samples were part of a research program in the Ceramics Division to analyze the chemical effects of different cutting fluids on ceramic machining [6]. Two samples were respectively ground using a commercial fluid (trade name Meqqem) and a NIST-developed organic fluid. When similar material removal rates ($\approx 1200\ \text{mm}^3/\text{min}$) prevailed during use of the two fluid types, very different tangential loads between sample and grinding wheel were observed. Subsequent profilometry scans revealed the same surface roughness, nominally $1\ \mu\text{m}\ R_a$, for each of the samples.

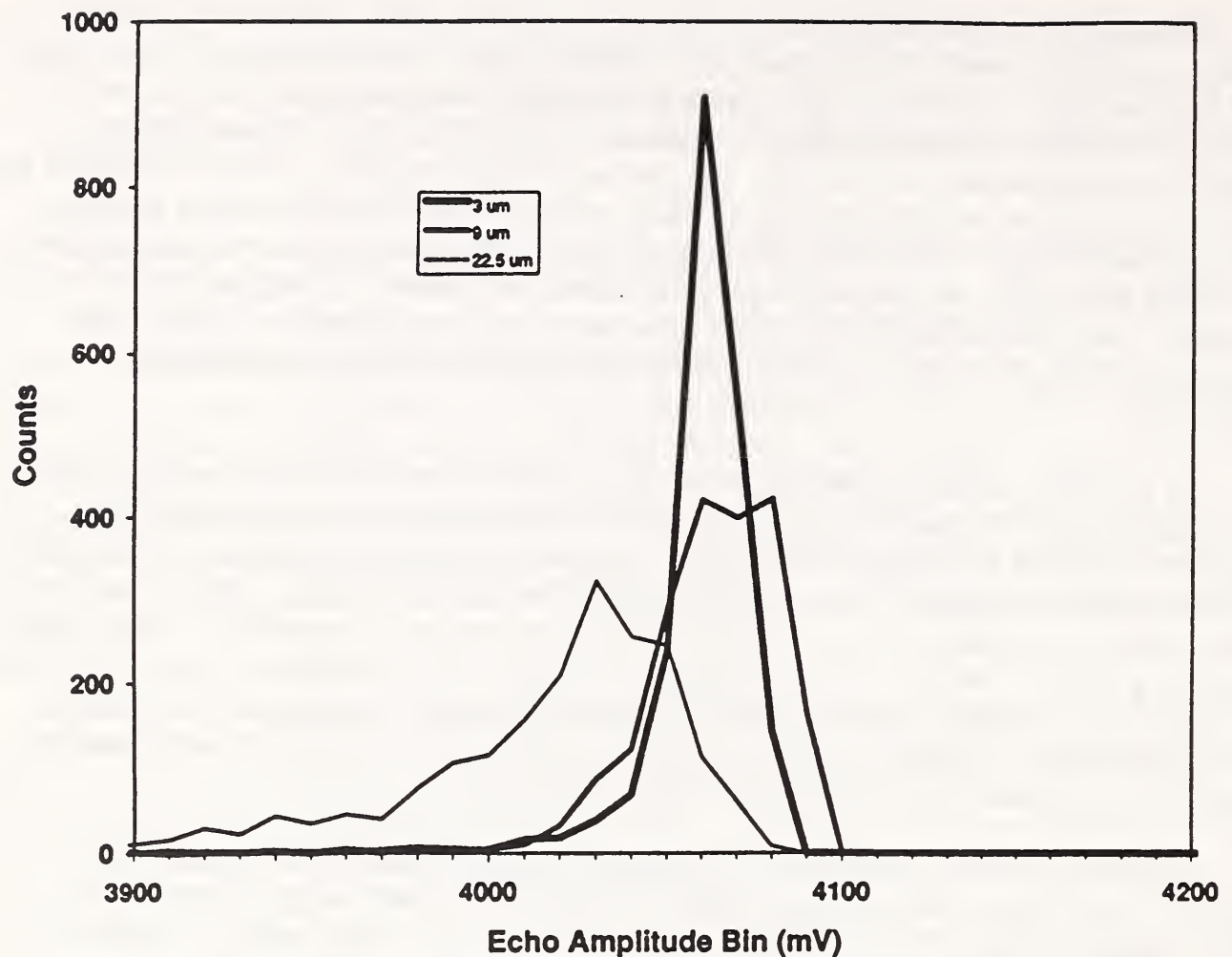


Fig. 1. Echo-amplitude distributions for ultrasonic scans taken on three smooth glass samples initially ground with respective grit sizes of 3, 9, and 22.5 μm .

Two subsequent nondestructive tests were then made to evaluate a possible contrast in the near-surface condition of the ceramic samples. Pulsed thermal-wave scanning revealed a significantly greater thermal diffusivity in the case of the sample/fluid for which the tangential load was less [7]. This greater thermal diffusivity was interpreted to indicate less subsurface damage with the lesser load. Ultrasonic scans at 30 MHz also revealed differences between the samples, with greater echo-amplitude values measured for the sample/fluid of lesser load. Figure 2 shows the echo-amplitude distribution for scans taken on these two samples. Since greater echo amplitude can be associated with a more rigid reflecting surface (due to lesser near-surface damage), there is corroboration with the thermal diffusivity results. On-going work includes thermal-wave and ultrasonic scans of these samples after complete removal of the near-surface damage.

We conclude that the ultrasonic results may be interpreted as revealing distributed near-surface damage in glass and ceramics. Sample sectioning may be performed to confirm whether there is such a correlation. Finally, we note that in this work equal-smoothness topographies allowed us to relate the ultrasonic signatures to different near-surface damage levels.

The authors are pleased to acknowledge Robert Polvani, Precision Engineering Division, NIST, for many helpful suggestions and discussions.

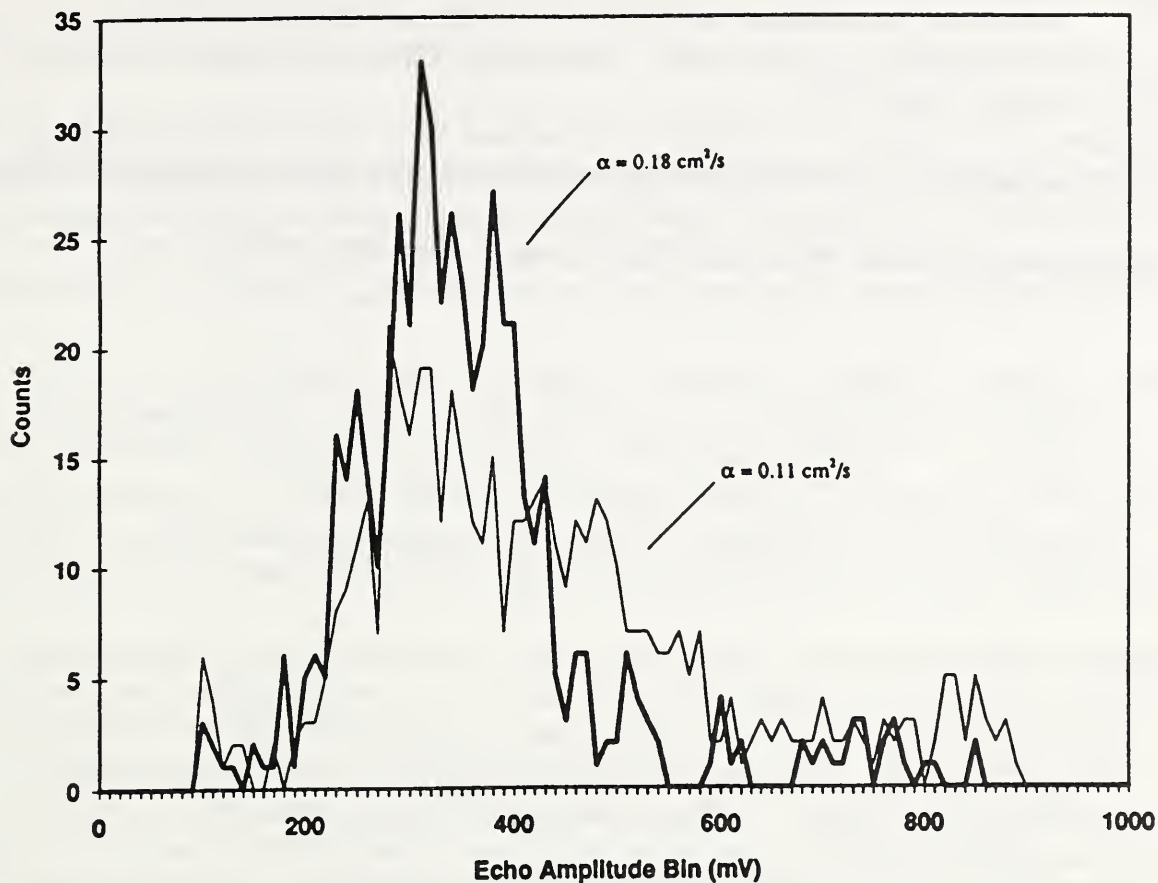


Fig. 2. Echo-amplitude distributions for ultrasonic scans taken on two silicon nitride samples ground using different grinding fluids but at the same material removal rate. The measured thermal diffusivity (α) of each sample is indicated.

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6. Personal communication: Tsi-Neng Ying and Stephen Hsu, Ceramics Division, NIST.
7. Measurements performed by Lanhua Wei, Ceramics Division, NIST.

Thermal Wave Evaluation of Ceramic Grinding Damage

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Ceramics Division, Materials Science and Engineering Laboratory

The objective of this work is to evaluate the feasibility of a thermal wave technique for nondestructive detection and characterization of grinding-induced damage in ceramics. The specific goals for this year were (1) to develop a better understanding of the thermal wave signal that results from machining damage and (2) to apply the thermal wave imaging complementary to various other techniques to investigate ground ceramic specimens.

Grinding is an extensively used technique for machining structural ceramics. However, grinding-induced damage is often a major factor limiting the strength and reliability of ceramic materials in engineering applications. Microcracks formed on and below the machined surfaces are a critical form of machining damage. Evaluation of this damage, preferably in a non-destructive manner, is therefore important for both fundamental study of material-removal mechanisms and manufacturing quality control of ceramic machining.

Substantial effort has been devoted to the development of non-destructive evaluation techniques, such as thermal waves [1,2] and ultrasonic detection [3,4]. The major difficulty in the application of these techniques to machining is due to the characteristic features (i.e., size, condition and location) of machining-induced microcracks. These microcracks extend to a few tens of micrometers below the machined surface. Detection of such damage requires an evaluation technique that has a high sensitivity to small subsurface microcracks, with a low sensitivity to the roughness of the machined surface. It is in this context that a thermal wave technique may be beneficial for characterization of grinding damage in ceramics, because of the effectiveness of microcracks in interrupting thermal waves.

The thermal wave technique used in this work is the optical beam deflection method (also called "mirage effect method"). The technique involves heating the sample surface with a focused, intensity-modulated laser beam. The heated region, in turn, heats the adjacent atmosphere, generating a gradient in the index of refraction. A probe laser beam passed through the heated atmosphere is refracted and the amount of the deflection of the probe beam is measured by a position-sensitive detector. The technique was upgraded in 1993 to state-of-the art capabilities, including both imaging and diffusivity evaluation modes operating in a wide thermal wavelength range.

Previous work [4] on detection of well-defined crack systems in ceramics using thermal wave imaging established the detectability of cracks with known forms. Based on these results, we further applied the technique to ground alumina specimens. Five polycrystalline alumina specimens with average grain sizes of 3, 9, 15, 21 and 35 μm were used. Grinding was performed on all the specimens with the same conditions. Figures 1a-1e show a series of thermal images taken on the ground surfaces of alumina samples with different grain sizes

(3, 9, 15, 21 and 35 μm). These images were prepared with the same contrast to allow a comparison among the signals. The thermal wave images in Figure 1 show darker spots corresponding to signals of larger amplitude generated as a result of localized high temperature regions. In order to interpret the source of the features shown in the thermal wave images, several examinations were conducted: (1) polished specimens (no machining damage) were examined as a reference to eliminate the possibility that the high temperature regions in Fig. 1 are associated with microstructural features of the original materials; (2) SEM micrographs taken from the same area on the ground surface were compared with the thermal wave image to confirm that the high temperature regions in the thermal wave images were not generated by surface related features such as grain pull-out; (3) different modulation frequencies were used to vary the thermal wave penetration depth in order to verify the depth of the thermal wave scatterers.

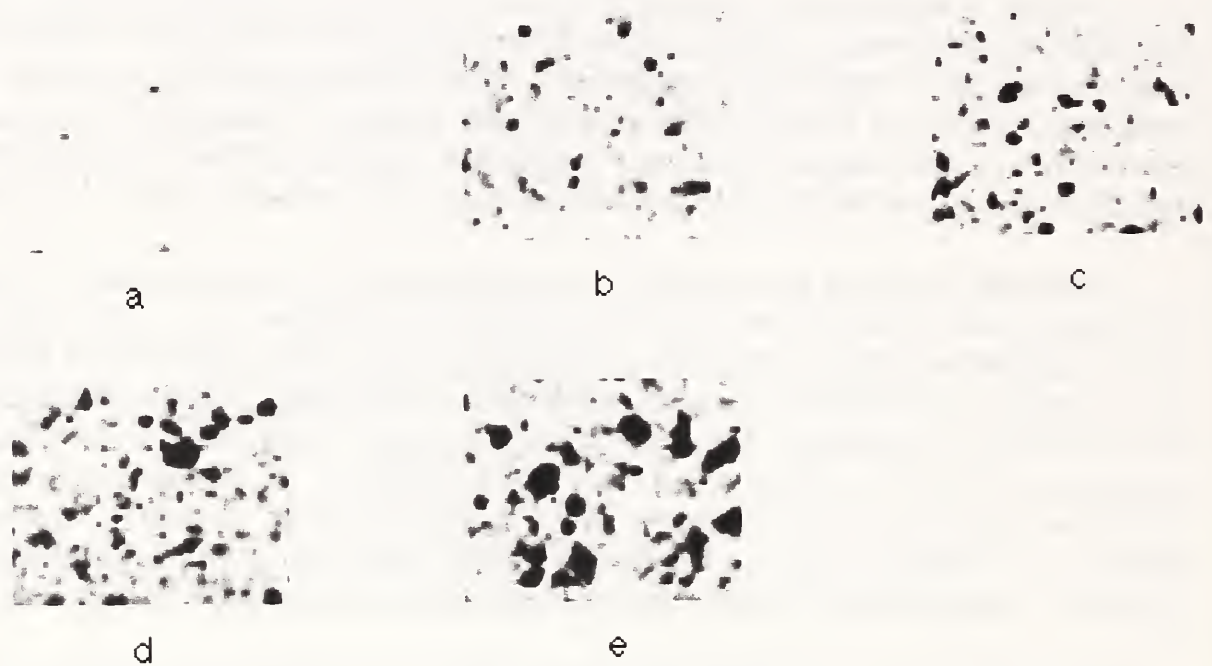


Fig. 1. Thermal wave images of ground alumina specimens with grain sizes (a) 3, (b) 9, (c) 15, (d) 21, and (e) 35 μm , showing that grinding-induced damage (dark spots) increases with grain size. The scan area of each image is 450 x 380 μm .

We concluded from these examinations that the features in the thermal wave images were dominated by the distribution of subsurface grinding-induced microcracks. The information obtained in Fig. 1 was further used to study the grain size effect on the mechanisms of material removal. Measurement of the area fraction of the dark spots in the thermal wave images shown in Fig. 1 can be used to estimate the density of grinding-induced subsurface microcracks. This was accomplished by first estimating the total area of the dark spots in a thermal wave image having a signal amplitude larger than a chosen threshold, and then dividing this value by the total area of the thermal wave image. The result of this calculation [5] indicated that the density of subsurface microcracks is related to the inverse square root of the grain size. This functional relationship agrees with the prediction of a microcracking

model. The thermal wave measurement showed its promising role in both detecting and quantifying grinding-induced subsurface microcracks in this study.

Another aspect of this research involved studying thermal wave response to integrated effects over microcracking zones in ceramics. Damage was generated using the Hertzian indentation test in which a hard sphere was loaded onto the surface of a silicon nitride specimen (conducted by Dr. Brian Lawn's group, MSEL) [6]. Local thermal diffusivities were measured over the damage zone and the virgin material. The difference in thermal diffusivity value between the damage zone and the virgin material was attributed to microcrack density. Using an existing theoretical model developed by Hasselman [7], microcrack density was quantified from local diffusivity measurements [6]. Results were compared with those obtained on the same group of silicon nitride material specimens using instrumented indentation, where the microcrack density was quantified by the shift of Young's modulus [8]. The two techniques showed the same functional relationship between Hertzian contact load and microcrack density.

The thermal wave imaging analysis results on both ground aluminas and contact damaged silicon nitrides demonstrated its usefulness in characterization of grinding-induced subsurface damage in ceramics. The study showed that the technique can be applied, complementary to other techniques, for both fundamental study of material removal mechanisms and detection of ceramic machining damage.

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Eddy Current Temperature Measurement During the Hot Rolling of Aluminum Sheet

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Arnold H. Kahn*

The objective of this project was the development of a non-contact method of measuring the temperature of aluminum sheet during the hot rolling process. Maintaining precise temperature control is necessary in order to achieve the desired mechanical properties and metallurgical state. Eddy current impedance measurements can determine the electrical resistivity of the material under test by non-contact electromagnetic induction of current in the material [1]. If the temperature dependence of the resistivity of the alloy of interest is known, an eddy current method can therefore determine the temperature during the processing. This has led to the current in-plant demonstration of an eddy current sensor for measuring resistivity and temperature in the hot mill at Alumax Mill Products in Lancaster, Pennsylvania. Our research in this project was conducted in cooperation with the Aluminum Association and its member companies.

The eddy current (EC) sensor for this application used a through-transmission coil. A primary coil excited eddy currents in the material under test; a secondary coil, on the opposite side of the aluminum sheet, received a signal dependent upon the response of the material. Measurements with this configuration were found to be insensitive to vertical displacement of the sheet. The effect of the velocity of the moving sheet on the sensor response was shown to be a higher order effect that could be neglected in this coil configuration at speeds below 5.08 m/s (1000 ft/min.) Typical speeds of 2.5 - 3.5 m/s (500-700 ft/min) were encountered in the actual mill environment. An impedance/ gain/phase analyzer determined the impedance of the coil system, i.e., the ratio of the secondary voltage to the primary current, and the relative phase angles of these quantities. These values were compared with the equivalent measurements in the absence of the test material. This process was repeated for each frequency of excitation. For example, we used 20 frequencies from 50 Hz to 200 Hz for a sheet of 3004 series alloy 2.4 mm (0.095 in) thick. The measurement, data processing, recording, and visual presentation were performed every 3 seconds.

From the impedance measurements, a computer program developed a curve of eddy current energy absorption versus frequency for the sheet under test. The curve for energy absorption was obtained from the real, or in-phase, part of the impedance. This curve has a characteristic peak which is a function of the resistivity of the material and the sheet thickness. Hence, by locating this peak and measuring the sheet thickness, the resistivity of the aluminum sheet was determined.

* Deceased

The temperature of the sheet was determined by applying Mathiessen's rule. The rule states that the resistivity of a low alloy material can be described as the sum of the temperature-dependent resistivity contribution from the predominant element and the constant "alloying" portion due to the alloying constituents. The contribution in resistivity due to the alloying components for these experiments was determined from quenched samples measured at room temperature for each data run, and was taken to be independent of temperature. Having isolated the resistivity due to alloying allows one to solve for the temperature as if the alloy were pure aluminum, with a constant additive shift. For aluminum, the resistivity as a function of temperature has been well established.

During the in-plant testing, the eddy current sensor was positioned at the exit of the final reducing rolls of the 3-stand hot mill as shown in Figure 1 [2]. The eddy current sensor data were collected along with other system parameters such as thickness and velocity of the sheet. The thickness was obtained from the on-line x-ray gauge positioned downstream from the eddy current sensor; the velocity was made available as a tachometer output voltage. Initially, a single wavelength infrared sensor was used as an additional measure of the sheet temperature, but proved to be unreliable due to variations in the sheet emissivity. The entrance temperature and the wrap-up temperature were measured with 2-point thermocouple probes and logged for later comparisons with the EC determinations.

A graph of the EC sensor output for a 3004 aluminum alloy at Alumax is shown in Figure 2. The temperature at the beginning of the run was 365 °C and decreased to 350 °C near the end of the billet due to radiative heat loss. The hot-rolling processing time for each billet was approximately 4 minutes. For comparison purposes, Figure 2 also shows the temperatures, measured by thermocouples, at the entrance to the hot-mill and on the final wrap-up once the product was coiled. The difference between the final EC temperature and the thermocouple wrap-up temperature was about 45 °C. This agrees qualitatively with the expected temperature difference for these two points in the process.

This eddy current sensor was operated for a four month period, October 1993 to January 1994, at Alumax Mill Products in Lancaster, Pennsylvania. During this time, the sensor ran successfully without any interruption in the normal production schedule. At the conclusion of the plant test, an error analysis was performed to identify the error sources and to determine the accuracy of the sensor. This process yielded an overall temperature uncertainty of 8.6 °C (3σ) when individual alloy correction measurements were made for each individual billet. However, if an average alloy correction was used for an entire alloy group (i.e. 3004 series) then a higher uncertainty, 12.4 °C, was estimated. As part of the error analysis, an ultimate expected error limit for the eddy current sensor system was formulated. Accounting for several system improvements, all of which are achievable, then an overall error of 6.5 °C (3σ) could be attained. This final estimate assumes that an additional eddy current sensor for measuring the conductivity of the individual sheets would be positioned at the entry of the mill to measure the alloy shift for each ingot. These modifications are currently being implemented with a final plant trial planned for 1995.

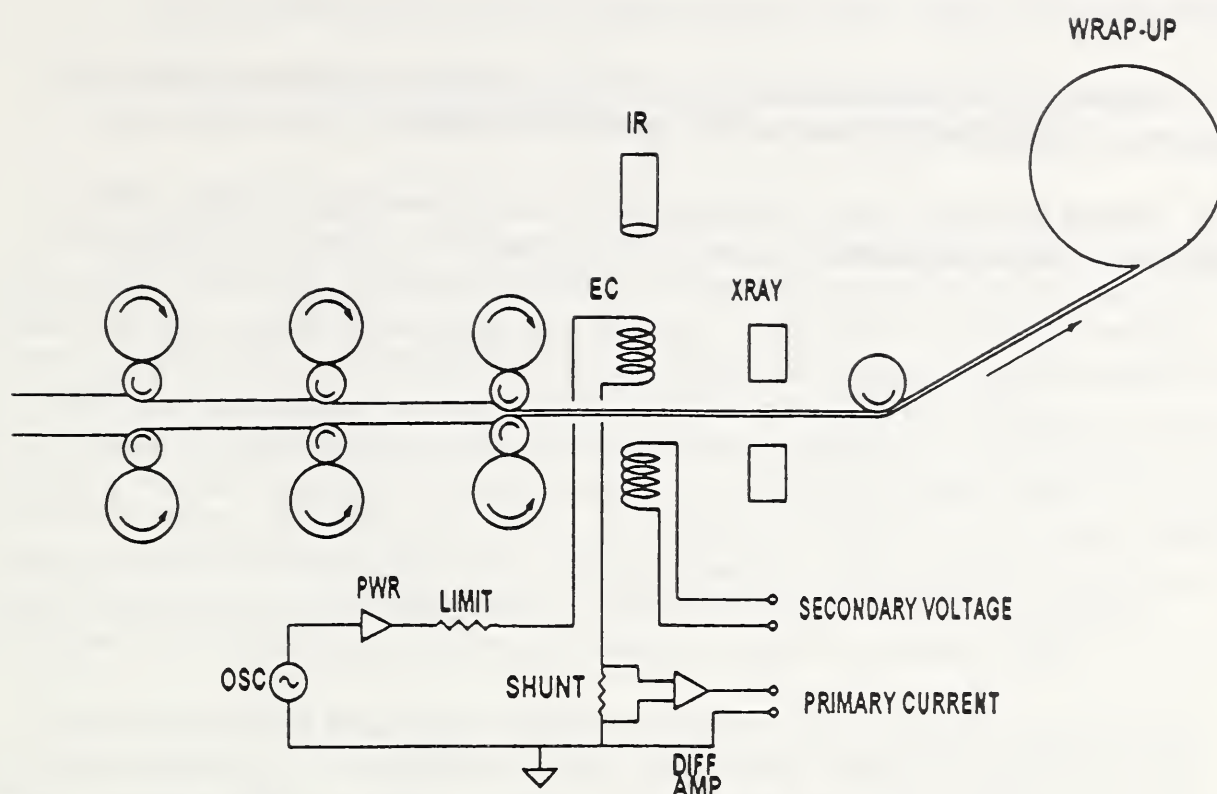


Fig. 1. Schematic of test configuration of the eddy current temperature sensor for hot-rolled aluminum sheet at Alumax Mill Products, Lancaster, PA.

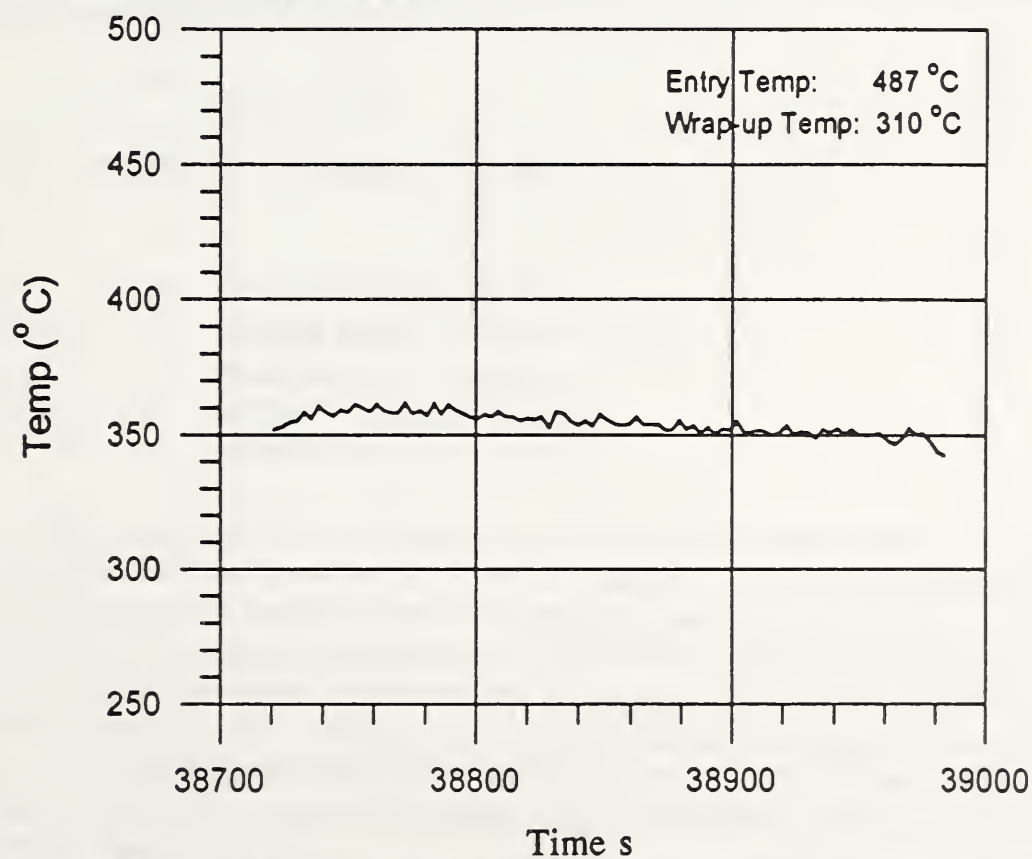


Fig. 2. Temperature versus time output from the eddy current sensor during the in-plant Alumax tests.

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IPM Metal Sensors for the Microstructural Engineering of Steels

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The Intelligent Processing of Materials (IPM) requires the establishment of quantitative relationships between the properties that appear in material specifications and the output of sensors that are monitoring the production process. In the case of steels, the strength properties are specified and the link with sensor outputs is made through the microstructure by establishing relationships between strength and the microstructure and between the microstructure and the sensor output. This study addresses the strength-to-microstructure link by developing models that predict the stress-strain curve of medium carbon steels at ambient temperature from a knowledge of the basic microstructural features of grain size, volume fraction of ferrite and the interlamellar spacing of pearlite. Given the stress-strain curve, the strength properties can be readily deduced. Other programs at NIST are applying Barkhausen noise and elastic wave velocity sensors to these low carbon steels.

The medium-carbon steels have a ferrite-plus-pearlite microstructure under normal processing conditions. The simplest and most widely used models to predict the yield strength (σ_y) and ultimate tensile strength (UTS) of a steel containing ferrite and pearlite come from the equations developed by Gladman et al. [1]. These equations use a simple modified law of mixture. The σ_y and UTS are expressed as

$$\sigma_y = \sigma_{y\alpha} f^{1/3} + \sigma_{yp} [1 - f^{1/3}] \quad (1)$$

$$\text{UTS} = (\text{UTS})_{\alpha} f^{1/3} + (\text{UTS})_{yp} [1 - f^{1/3}] \quad (2)$$

where

$\sigma_{y\alpha}$	=	yield strength of ferrite,
$(\text{UTS})_{\alpha}$	=	ultimate tensile strength of ferrite,
σ_{yp}	=	yield strength of pearlite,
$(\text{UTS})_{yp}$	=	ultimate strength of pearlite,
f	=	volume fraction of ferrite.

$\sigma_{y\alpha}$ and $(\text{UTS})_{\alpha}$ are a function of chemistry and ferrite grain size, while σ_{yp} and $(\text{UTS})_p$ are a function of chemistry and pearlite interlamellar spacing. The development of the Gladman equations was based on results of regression analysis on data from tests on ferrite-plus-pearlite steels with different compositions. They neither correlate to any physical phenomena during deformation nor predict the complete stress-strain curves. The Gladman equations only predict two points in a stress strain curve, namely, the yield strength and the ultimate tensile strength. A complete stress-strain curve not only gives values of σ_y and UTS, but also reveals the detail of the deformation process, such as hardening characteristics and the change of the steel's structure.

To predict the complete stress-strain curve of a ferrite-plus-pearlite steel in a tension test, the detail of how the strain is partitioned into ferrite and pearlite during deformation must be considered [2] which is lacking in the Gladman's analysis. Two cases that treat the strain partition are considered here.

- Case 1: Ferrite deforms plastically while pearlite remains elastic. This case applies when ferrite is the continuous phase (pearlite is discontinuous) and the applied strain is not large enough to cause pearlite to deform plastically.
- Case 2: Both ferrite and pearlite deform plastically and applied strain is partitioned equally into ferrite and pearlite: the equal-strain model. This case applies when the volume fraction of pearlite is large and the strength difference between ferrite and pearlite is relatively small.

The key ingredients to the two analyses are (1) the flow curve of ferrite, (2) the flow curve of pearlite, and (3) the strain partition ratio in case 1. The strain partition ratio is defined as the ratio of total strain in ferrite over total strain in pearlite. The flow curves (the plastic deformation portion of the stress-strain curves) of ferrite and pearlite are described in Eqs. (3) [3] and (4) [4], respectively, and the strain partition ratio is given in Figure 1.

$$\sigma = a_s (b_s + \epsilon_p)^{N_s}, \quad (3)$$

$$\sigma = \sigma_v - K_v \exp(n_v \cdot \epsilon_p), \quad (4)$$

where

$$\begin{aligned} a_s \text{ (in MPa)} &= 109[\text{Si}] + 62.7[\text{Mn}] + 10.8 d^{0.5} + 373, \\ b_s &= 0.002, \\ N_s &= -0.037[\text{Si}] - 0.011[\text{Mn}] + 0.219 d^{0.5} - 0.12, \\ \sigma_v \text{ (in MPa)} &= 637 + 67/S_p, \\ K_v \text{ (in MPa)} &= 500, \\ n_v &= -42.4. \end{aligned}$$

The quantity [X] represents the mass percentage of element X and S_p is the pearlite interlamellar spacing.

The detailed procedures for performing the analyses under Cases 1 and 2 were published [1]. One of the results is shown in Figure 2. As shown in Figure 2, it can be concluded that there is good agreement between the predictions and the experimental data. The models that treat Case 1 and Case 2 can be used to predict the complete stress-strain curve of medium-carbon steels, from which the strength properties can be estimated, and to guide the development of process control sensors and systems. Future studies will focus on relating the processing parameters that control the evolution of microstructure to on-line measurables so that intelligent processing can be implemented.

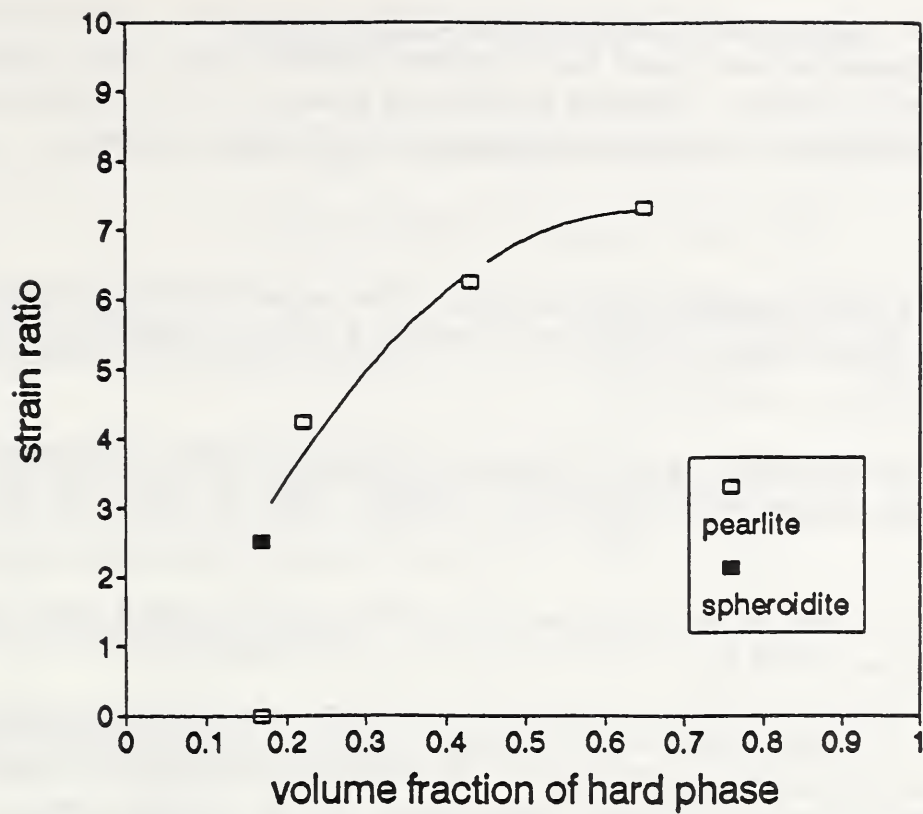


Fig. 1. Strain partition ratio as a function of pearlite.

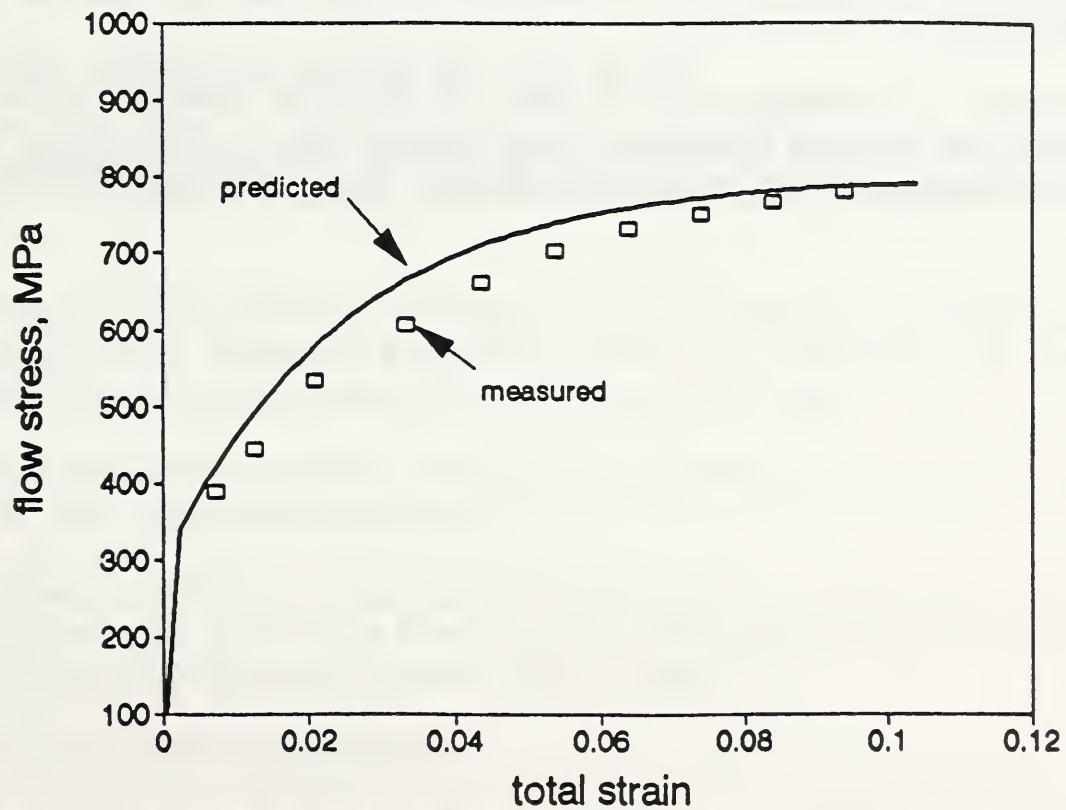


Fig. 2. True stress vs. true strain curve for a 0.4% carbon steel. Comparison of prediction results with experimental data.

In the course of this study, extensive interactions with the steel industry were maintained. Chrysler Motors Corporation and Inland Steel Company provided many of the materials and data on their processing histories. Through students and faculty at the Colorado School of Mines, these new models are now being implemented at the Timken Company.

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PUBLICATIONS

P. T. Purtscher, Y. W. Cheng, and R. P. Foley, "Prediction of Strength Properties for Plain Carbon and Vanadium Microalloyed Ferrite-Pearlite Steel," in Proc. of the 36th Mechanical Working and Steel Processing Conference, Oct. 16-19, 1994, Baltimore, MD.

OIPM PERSONNEL AND ACTIVITIES

The staff of the Office of Intelligent Processing of Materials is listed below.

OIPM STAFF IN FISCAL YEAR 1994

Dale Hall, Chief
George Birnbaum, Senior Scientist

Patty Salpino, Administrative Officer
Ellen Altman, Secretary
Linda Souders, Secretary

Dr. Robert Schaefer of the Metallurgy Division served as a part-time staff member. Dr. Sharon Glotzer joined the staff of OIPM as the Deputy Chief, Center for Theoretical and Computational Materials Science on January 20, 1995.

A. OIPM SEMINARS AT NIST

Julian Szekely, Massachusetts Institute of Technology, Cambridge, MA, "Mathematical Modeling and the Intelligent Processing of Materials," April 1, 1994.

Renee M. Kent, Wright Laboratory, Wright Patterson Air Force Base, OH, "Quantitative Analysis on Fibers and Composites for Intelligent Processing Applications," June 8, 1994.

B. INVITED TALKS AND PAPERS BY OIPM STAFF

"The Far Wings of Allowed and Collision Induced Lines," G. Birnbaum, 12th International Conference on Spectral Line Shapes, June 16, 1994, University of Toronto, Toronto, Canada.

"The Wings of Pressure Broadened Molecular Bands," G. Birnbaum, in Spectral Line Shapes, Vol. 8, AIP Conference Proceedings, edited by A. David May, J. R. Drummond and Eugene Oaks, American Institute of Physics, New York, 1994.

"Eddy Current Research at NIST for Monitoring," G. Birnbaum, 41st Sagamore Conference, August 29, 1994, Plymouth, Massachusetts.

"Sensor Research at NIST for Measuring Process Parameters," G. Birnbaum, Advanced Technology Program: Sensors and Control Systems, The Requirements of U.S. Industry - Focused Program Development Workshop, May 23, 1994.

C. NIST SPONSORED WORKSHOPS

Consortium on Casting of Aerospace Alloys Annual Meeting, May 4-5, 1994.

D. COMMITTEES, CONFERENCES, AWARDS AND APPOINTMENTS

Dale Hall

The Electrochemical Society

Technical Affairs Committee

Society Meeting Committee

Advisor, Energy Technology Division

Advisor, Luminescence and Display Materials Division

Executive Committee, Industrial Electrolysis and Electrochemical
Engineering Division

Chairman, ad hoc Committee on Meeting Content and Format

Electronic Communications Task Force

Co-organizer, Symposium on Concurrent Engineering for Electrochemical and Solid State Applications, May 1995.

Steering Committee, Symposium on Smart Processing of Materials, co-sponsored by MRS/SAMPE, October 1995.

Advisory Board, University of Connecticut Environmental Research Institute Critical Technology Program.

George Birnbaum

Associate Editor, Research in Nondestructive Evaluation

Research Council, ASNT

Organizer and Co-chairman, ASNT Advanced School on Sensors for Process Monitoring and Quality Control, June 1995.

National Institute of Standards and Technology

Organizational Chart

